Ozone

Method number	1
Application	Air analysis
Analytical principle	Photometry
Completed in	May 1992

Summary

The method described for the determination of ozone is based on the method proposed by the VDI for monitoring ambient air. The VDI [1,2] method is also suitable to determine airborne ozone at the workplace. Ozone-containing air is drawn through two serially connected wash bottles equipped with frits. The decolourization of the indigo carmine solution is measured by use of photometry within 5 min.

Standard deviation (rel.)	s = 9.7%
Mean variation	u = 21.6%
where $n = 11$ determinations	and $c = 0.2 \text{ mg/m}^3$
Reciprocal calibration factor	$k' = 16.72 \ \mu g$ (referring
to 25 mL measuring solution	and 5 cm cuvettes)
$0.85 \ \mu g \text{ ozone} = 0.011 \ \text{mg/m}$	3
up to 2 h	
80 L	
	Standard deviation (rel.) Mean variation where $n = 11$ determinations Reciprocal calibration factor to 25 mL measuring solution 0.85 µg ozone = 0.011 mg/m up to 2 h 80 L

Ozone

Ozone (O₃) is an unstable, pungent smelling, extremely toxic gas (molecular weight 48.0 g/mole; melting point -192.5 °C; boiling point -111.9 °C). Ozone is one of the strongest oxidation agents. It is readily soluble in alcohol and oils.

In a height of 15-25 km ozone is formed of oxygen under the influence of UV rays. At ground levels concentrations of 0.02–0.05 ppm are measured. In addition it is formed during industrial processes which generate great intensities of UV rays (e. g. arc welding).

Ozone is used in the bleaching of oils, synthetic fibres, paper, cellulose and textiles. The most important range of application is the processing of drinking water according to DIN 19627.

Ozone is listed in the carcinogenic category III 3 [3]. The currently valid TRK value (1998) is 0.2 mg/m^3 and 0.1 mL/m^3 [4].

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1 General principles

The method described for the determination of ozone is based on the method proposed by the VDI for monitoring ambient air. The VDI [1,2] method is also suitable to determine airborne ozone at the workplace. Ozone-containing air is drawn through two serially connected wash bottles equipped with frits. The decolourization of the indigo carmine solution is measured by use of photometry within 5 min.

2 Equipment, chemicals and solutions

2.1 Equipment

Pump, pumping capacity 40 L/h Ozone generator Gasmeter Photometer suitable to measure in the wavelength of about 623 nm Wash bottles with frits 2 or 5 cm Cuvettes 25 mL Bulb pipette 500, 1000 mL Volumetric flasks 100 mL Graduated cylinder Polytetrafluoroethylene (PTFE) hoses Stopwatch Thermometer Barometer

2.2 Chemicals

Indigo carmine, analytical grade, disodium salt of the 5,5'-indigosulfonic acid Disodium phosphate, analytical grade, $Na_2HPO_4 \cdot 12 H_2O$ Monopotassium phosphate, analytical grade, KH_2PO_4

2.3 Solutions

Solution I:

In a 1000 mL volumetric flask 28 g Na_2HPO_4 · 12 H₂O and 80 g KH₂PO₄ are dissolved in distilled water and diluted to the mark with distilled water. The pH-value of the solution is adjusted to 5.5.

Solution II:

In a 500 mL volumetric flask 150 mg indigo carmine are completely dissolved, 50 mL of solution I are added and the solution is diluted up to the mark with distilled water.

Solution III:

20 mL of solution II and 100 mL of solution I are mixed in a 1000 mL volumetric flask and diluted up to the mark with distilled water. For the analysis the solution has to be freshly prepared. The shelf life of the solution is 24 h.

3 Calibration

The method is calibrated by parallel measurements according to the basic method [2]. The generation of the ozone containing air occurs by means of an ozone generator. The measurements are carried out as described in Sect. 4. The ozone concentration is adjusted at the ozone generator; different calibration concentrations can be adjusted by varying the sampling times. The decolourization of the indigo carmine solution of **both** wash bottles is measured.

From the sum of the decolourization $\Sigma \Delta E = \Delta E_1 + \Delta E_2$ with $\Delta E_1 = E_{0,1} - E_1$ and $\Delta E_2 = E_{0,2} - E_2$ the decrease of the extinction is plotted against the absolute ozone quantity to obtain the calibration curve.

The calibration curve was made for the range of 1–12 µg ozone. The calibration factor – referring to a 5 cm cuvette – is $k = 0.0598 \mu g$, the reciprocal calibration factor is $k' = 16.72 \mu g^{-1}$. The correlation coefficient of the calibration curve is r = 0.995. An example of a calibration curve is shown in Fig. 1.

4 Sample collection and analytical determination

25 mL each of solution III are transferred into two serially connected wash bottles with frits (cf. Sect. 2.3) and installed in the sampling device (cf. Fig. 2). By a flow-stabilized pump or a pump controlled by a gasmeter a flow rate of 40 L/h is applied (sampling time up to 2 h). If higher concentrations are observed (rapid decolourization of the solution) the sampling time has to be reduced.

After the sampling the wash bottles are closed airtight and analysed within 5 min. In the laboratory the solutions are transferred separately into 5 cm cuvettes and the decolourization is determined.

Under the conditions as described the absorption in the first wash bottle is greater than 90%.

5 Calculation of the analytical result

For the calculation of the airborne ozone concentration at the workplace the following equations are applied:

 $\rho = \frac{\Sigma \varDelta E \cdot k'}{V_Z} \cdot \frac{273 + t_g}{273 + t_a}$

At 20 °C and 1013 hPa:

The corresponding concentration by volume σ – independent of pressure and temperature – is:

$$\sigma = \rho_0 \frac{24.06 \text{ L/mole}}{48.00 \text{ g/mole}}$$

$$\sigma = \rho \cdot \frac{273 + t_a}{p_a} \cdot \frac{1013 \text{ hPa}}{293} \cdot \frac{24.06 \text{ L/mole}}{48.00 \text{ g/mole}}$$

At $t_a = 20 \text{ °C}$ and $p_a = 1013 \text{ hPa}$:

$$\sigma = \rho \cdot \frac{273 + t_a}{p_a} 1.733 \frac{\text{hPa} \cdot \text{mL}}{\text{mg}}$$

$$\sigma = \rho \cdot 0.501 \, \frac{\mathrm{mL}}{\mathrm{mg}}$$

-	
$\Sigma \Delta E = \Delta E_1 + \Delta E_2$	Sum of the decrease of the extinction of the indigo carmin solutions
k'	Reciprocal calibration factor in mg
V_Z	Sample volume in m ³
t _a	Temperature of the ambient air in °C
t _g	Temperature in the gasmeter in °C
$p_{\rm a}$	Pressure of the ambient air in hPa
ρ	Airborne ozone concentration by weight in mg/m ³ referring to t_a
	and $p_{\rm a}$
$ ho_0$	Airborne ozone concentration by weight in mg/m ³ referring to
	20°C and 1013 hPa
σ	Airborne ozone concentration by volume in mL/m ³

6 Reliability of the method

6.1 Precision

To test the reproducibility of the method defined ozone concentrations were adjusted at the ozone generator and drawn through the absorption solution. The concentrations 0.1 mg/m^3 , 0.2 mg/m^3 and 0.4 mg/m^3 were applied (cf. Tab. 1).

Concentration mg/m ³	Number of individual measurements <i>n</i>	Standard deviation (rel.) <i>s</i> %
0.1	12	16.5
0.2	11	9.7
0.4	9	11.2

Table 1. Standard deviation (rel.) s.

6.2 Determination of the blank value and the quantification limit

The quantification limit for ozone was calculated from the standard deviation of the blank value $M_b = E_0$ as follows:

 $C = M_{\rm b} + \beta s_0$

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- *C* Relative quantification limit
- s_0 Standard deviation of the blank value
- $M_{\rm b}$ Average blank value

The values $M_b = 1.1286$ and $s_0 = 0.0067$ were determined from a total number of 16 individual measurements. This leads to an absolute quantification limit of 0.85 µg ozone. The relative quantification limit is 0.011 mg/m³ for a 80 L sample volume.

6.3 Specificity

The method has no cross sensitivity to SO_2 . The presence of NO_2 effects slightly higher concentration values.

6.4 Shelf life

The time between sampling and analysis should not exceed 5 min.

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Fig. 1. Calibration curve $(\Sigma \Delta E = \Delta E_1 + \Delta E_2)$.



Fig. 2. Calibration apparatus.

- 1 Ozone generator
- 2 Wash bottles with frits
- 3 Gasmeter
- 4 Manometer
- 5 Thermometer
- 6 Pump