

## An Evaluation of the Ehmert Technique for Measuring Ozone Profiles in the Atmospheric Surface Layer

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An evaluation is made of the resolution of a modified Ehmert apparatus for measuring ozone profiles in the atmospheric surface layer. Comparisons between instruments suggest a resolution capability for difference measurements by two instruments of the order of  $\pm 1.4 \mu\text{g m}^{-3}$  of ozone. Typical differences in ozone concentration between 16- and 1-meter height are observed to be 3–4  $\mu\text{g m}^{-3}$  during conditions of strong daytime mixing. It follows that the Ehmert method may be used to measure ozone differences and determine ozone fluxes during representative atmospheric conditions; such measurements have hitherto been considered impractical.

### INTRODUCTION

Ozone budgets have been used by *Junge* [1962] and *Newell* [1963] to study general circulation and stratospheric-tropospheric exchange problems. The ozone destruction rates or flux values that are necessary for the determination of ozone budgets have not yet been comprehensively measured. The required fluxes near the earth's surface can be obtained by the profile method, first used by *Regener* [1957]. The resolution of the instruments [*Desjardins*, 1967; *Ehmert*, 1959; *Nash*, 1967; *Regener*, 1964; *Stair*, 1959] that can be used for such work is not very high when compared with the ozone differences and therefore needs to be carefully assessed.

*Aldaz* [1969] has presented an extensive set of ozone flux values. However, as described by *Regener and Aldaz* [1969], these flux values have been inferred from measurements of the earth's chemical reactivity, owing to the difficulties they experienced in measuring ozone profiles at diffusivities above  $1000 \text{ cm}^2 \text{ sec}^{-1}$ . The method described below has been used for diffusivities of up to 10 times this value, which corresponds to a more demanding range of atmospheric conditions.

In this paper the modified Ehmert ozone measuring apparatus [*Ehmert*, 1959] is described, and the resolution of the instrument is then evaluated. Results are presented from measurements of ozone profiles made with two

such instruments. The technique is only suitable for use in unpolluted environments.

### DESCRIPTION OF THE METHOD

Detailed descriptions of the Ehmert technique are given by *Ehmert* [1959] and *Warmbt* [1964]. Air is bubbled through a solution containing iodide ions, which react with the ozone in the air. The iodine produced reacts completely with sodium thiosulfate in the solution. The ozone amount is found from comparing the thiosulfate content of bubbled and unbubbled solution by electrochemical titration.

There can be three sources of inaccuracy in such measurements: (1) errors in the air volume measurement, (2) variations in the efficiency of absorption of ozone in the solution and losses in transferring the solution to the titration apparatus (these errors are not measured in this work), (3) errors in the thiosulfate titration measurement.

The stoichiometry of the ozone iodide reaction (i.e. the ratio of iodine produced to ozone reacted) has been examined by *Saltzman and Gilbert* [1959]. For neutral buffered 1% potassium iodide solution and ozone concentrations above 2 ppm, it is unity. At lower ozone concentrations, in the range used here, the stoichiometry may be 5% less, but this will not significantly alter the measured ozone differences.

### EQUIPMENT

*Chemicals.* Analytical grade chemical reagents and distilled water from an all-glass

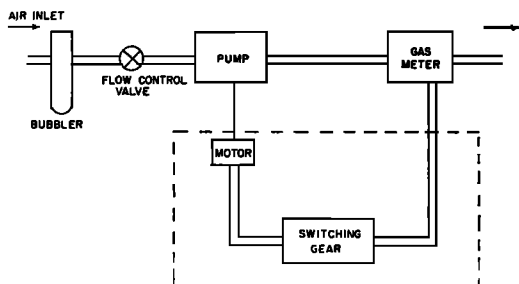


Fig. 1. Flow diagram of air meter.

still are used. The 1% potassium iodide solution is made of 5-gram KI, 0.53-gram  $\text{Na}_2\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , and 0.59-gram  $\text{Na}_2\text{H}_2\text{PO}_4$  dissolved in 500-ml distilled water. To the KI solution is added 1.5 ml of 0.25-gram  $\text{Na}_2\text{S}_2\text{O}_8$  in 100 ml distilled water. For each observation 10 ml of the resulting solution is used in the bubbler.

**Air-metering equipment.** A flow diagram of the air-metering equipment is shown in Figure 1. A dry gas meter (Smith's DO, 7) is used for the volume measurement. A microswitch in the pump motor circuit is attached to the gas meter indicator dial giving the air volume control of 2 ft<sup>3</sup> per observation. The meters give mean values of the air volume to within 0.01 ft<sup>3</sup> and have standard deviations of 0.02 ft<sup>3</sup> for individual observations. Flow rates of 1.4 to 1.9 liters per minute (3 to 4 ft<sup>3</sup> per hour) are used.

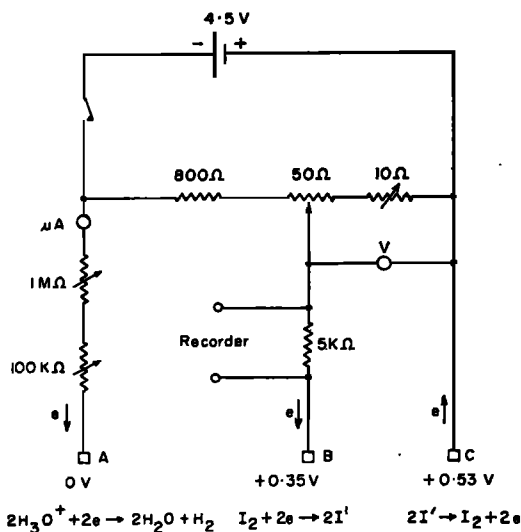


Fig. 2. Titration unit, with electrodes A, B, and C. Electrodes A and C supply the titrating current, B and C are the sensing electrodes.

The air meter is connected to the bubbler by 1/4" ID reinforced air hose. The almost rigid walls of this air hose allow negligible volume contraction over its length and offer a minimum of air resistance in spite of its 30-meter length.

**The titration unit.** The circuit of the titration unit, which is used with a magnetic stirrer, is shown in Figure 2. Suitable titration units are also described by *Ehmert* [1959] and *Lingane* [1958]; *Lingane* also gives an account of the physics and chemistry involved. Large surface area sensing electrodes, 1.5 × 2.1 cm, ensure the required accuracy (~1/2%) in determining the titration end point.

**The bubbler.** The bubbler, shown in Figure 3, follows the design recommended by *Thorpe* [1954] and *Silber* [1962]. There is no fritted glass, which might catalytically destroy ozone. Also, the bubbler produces fine bubbles of air in the solution, ensuring that all the ozone reacts.

The glass surfaces in contact with the solution must be free of any ozone or iodine-reacting substances. Before use and after every twenty measurements the bubblers are cleaned and placed in an ozone atmosphere for about twelve hours. The first observation made after this process is discarded. Pipettes, beakers, and the electrodes are also cleaned at this frequency.

#### INSTRUMENT COMPARISONS

Sixty comparisons have been made in the field with various sets of the new apparatus. The results give a standard deviation between two instruments of  $\pm 1.4 \mu\text{g m}^{-3}$  ozone concentration. Figure 4 and Table 1 show comparisons

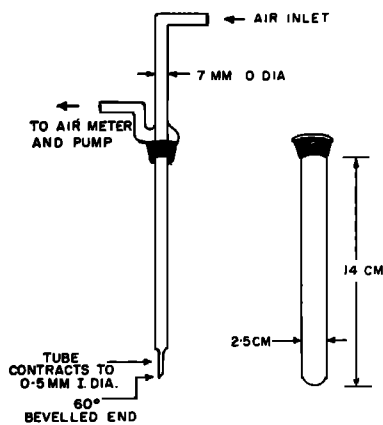


Fig. 3. Ozone bubbler.

between two sensors; Table 2 is from the comparison of four sensors.

Table 1 also shows the limiting factors in the instrument's resolution, as discussed above. This version of the Ehmert apparatus compares favorably with that described by *Warmbt* [1964], the two having standard errors of  $\pm 1.4$  and  $\pm 3 \mu\text{g m}^{-3}$ , respectively. The improvement is due to the use of larger air volumes and more accurate titrations.

The calibration coefficients shown in these figures and tables correct each sensor reading, so that, within the resolution, all the sensors give the same result when compared. If the assumption is valid that the mean of the observations for comparison is the true ozone value, the calibration coefficient is the multiplicative factor that brings the observations of a particular sensor into best fit with the true ozone values. The standard deviation of the residual discrepancies is the measure of the instrument's resolution. The correction factor may be caused by variations in the ozone collection efficiency of the individual bubblers or by minute air leaks in the different pumping apparatus.

#### PROFILE MEASUREMENTS

Twenty-seven observations of ozone gradients between the 1- and 16-meter levels were made using two Ehmert instruments at the Edithvale site as described by *Swinbank* [1955]. Observations were made between 1100 and 1600 local time from July to September 1968. The results are presented in Table 3 together with the mean wind speeds on the 1-meter level, which indicate conditions of strong mixing.

Of the observed differences in ozone concentration, 80% are  $2 \mu\text{g m}^{-3}$  or larger, which can be satisfactorily resolved by individual meas-

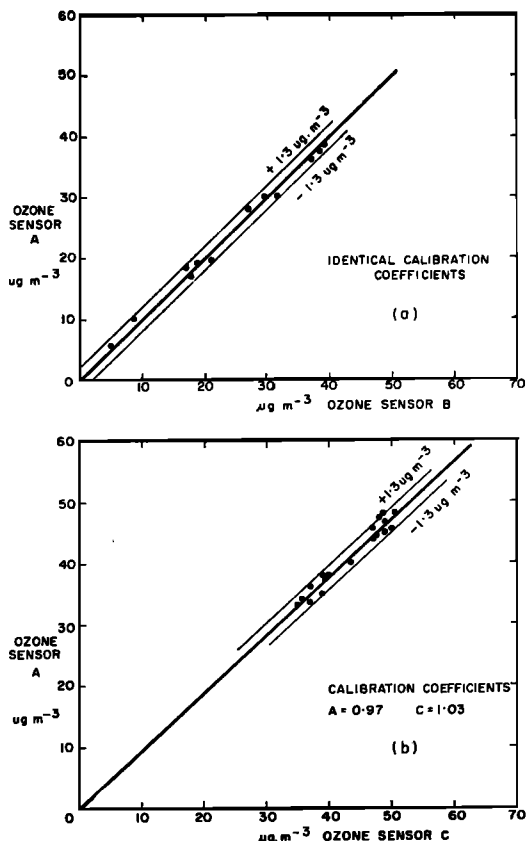


Fig. 4. Comparisons of two ozone sensors: (a) sensors A and B, which have the same calibration coefficients, (b) sensors A and C, which have calibration coefficients of 0.97 and 1.03, respectively.

urements. However, if the resolution of the instruments had been slightly worse, from Table 3 we can see that a considerable number of the ozone differences would not have been observable. Smaller differences can be resolved with

TABLE 1. An Analysis of the Instrument Errors and a Comparison of Two Ozone Sensors

Source of Error	No. of Observations	Mean	Std. Deviation	% Accuracy	Absolute Accuracy Ozone Concentration
Air volume	47	2.008 ft <sup>3</sup>	0.02 ft <sup>3</sup>	1	<0.6 $\mu\text{g m}^{-3}$
Ozone absorption	Not measured	...	...	...	...
Titration	10	643 sec	4 sec	0.5	<0.3 $\mu\text{g m}^{-3}$
Inter-comparison of two instruments	60	$\sim 40 \mu\text{g m}^{-3}$ ozone concentration	1.4 $\mu\text{g m}^{-3}$	3	1.4 $\mu\text{g m}^{-3}$

TABLE 2. The Results of Ten Comparisons of Four Ozone Sensors

Sensor	Calibration Coefficient	Standard Error of Calibration Coefficient			Standard Deviation, $\mu\text{g m}^{-3}$
1	1.01	$\pm 0.01$			1.5
2	0.96	$\pm 0.01$			1.4
3	1.01	$\pm 0.01$			1.0
4	1.03	$\pm 0.01$			1.1
<i>Scatter of Results</i>					
Deviation $\mu\text{g m}^{-3}$	0	0.5	1.0	1.5	2.0
No. of observations	13	16	9	1	1

this method by using the mean of several observations.

Two negative ozone gradients of  $-3.5$  and  $-0.5 \mu\text{g m}^{-3}$  were observed during a time of rapid decrease of surface ozone concentration. These gradients were supported by a Mast Brewer ozonesonde observation and are considered to be the effect of a pollutant in the air rather than of malfunctioning instruments.

#### CONCLUSION

Comparing two sets of Ehmert apparatus, a resolution of  $\pm 1.4 \mu\text{g m}^{-3}$  ozone concentration for difference measurements is obtained. Some ozone profiles measured from 16 to 1 meter during conditions of strong daytime mixing give average differences of 3 to 4  $\mu\text{g m}^{-3}$ . This result indicates that ozone profiles can be measured by this method during representative conditions of atmospheric mixing, a hitherto unattained goal. The ability to make daytime measurements of ozone profiles, and thereby ozone fluxes, is important because daytime is the period of maximum coupling of the free atmosphere and the earth's surface and, thus, is the time when we

TABLE 3. Some Ozone Difference Measurements between 16- and 1-Meter Height

	Ozone Difference, $\mu\text{g m}^{-3}$						
	1	2	3	4	5	6-10	11-20
Number of occurrences	5	4	6	5	2	1	2
Percentage of occurrences	20	16	24	20	8	4	8
Wind speed 1-m level $\text{msec}^{-1}$	4.1	4.8	6.0	5.3	5.0	1.8	2.8

would expect the most efficient ozone exchange. The daytime is probably much more important than the nighttime when considering ozone destruction at the earth's surface.

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