Chemiluminescent Ozone Instrument for Aircraft Observation

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Abstract

An ethylene-ozone chemiluminescent instrument has been modified so that it can control the sample and ethylene flow rates irrespective of the ambient pressure and temperature. Through detailed laboratory tests the following characteristics have been found.

(1) The sensitivity of the instrument is highly dependent on the sample mass flow rate as expected from the chemiluminescent reaction scheme. (2) The change in sensitivity as a function of the ethylene mass flow rate is much less. (3) The error associated with the stability of the zero level and the standard deviation from a linear relationship is less than 1 ppbv. (4) The change in the sensitivity for pressures between 1000 and 500 mb is insignificant. A larger reduction in sensitivity at lower pressures necessitates corrections based on the calibration curve obtained. It amounts to about 10% at 400 mb under optimum flow conditions.

Aircraft observations of ozone up to the altitude of 6 km have been made. The flow control system has proved to maintain the flow rates constant to within 3% on board the aircraft. Ozone mixing ratios obtained by this experiment are also reported.

1. Introduction

For the measurements of atmospheric ozone at the ground, commercial UV photometers and chemiluminescent ozone instruments are commonly used. However these instruments usually cannot be used for aircraft observations without some design changes due to different environmental conditions. For the measurement of ozone on board an aircraft by modified commercial UV and chemiluminescent instruments, Routhier *et al.* (1980) adopted a system which involved a pressure regulation of air sampled. Gregory *et al.* (1983a, b, 1984) also modified a commercial chemiluminescent ozone instrument and used it to make aircraft measurements. One of the most important features of the latter

chemiluminescent instrument is that the sensitivity of the instrument in terms of ozone mixing ratio is almost independent of the ambient pressure, at least down to about 650 mb. The chemiluminescent technique that compensates for the pressure changes can be considered as one of the promising methods for the accurate determination of the ozone concentration in the free troposphere. However, for any extended use of this type of instrument and for further improvement in its precision, more detailed investigations of the characteristics of the instrument are necessary. Therefore, as a first step, we have also modified a commercial ozone instrument and performed tests with it in the laboratory and we have also made aircraft observations with it. This paper gives a description of these laboratory and field tests.

2. Ozone instrument

The principle of the measurement of the chemiluminescent ozone instrument is based on the chemiluminescent reactions between ozone and ethylene (Finlayson *et al.*, 1972; Aïmedieu and Barat, 1981; Mehrabzadeh *et al.*, 1983; O'Brien *et al.*, 1983). In the reaction chamber, ethylene is mixed with sampled ambient air which contains ozone. The chemiluminescence is measured with a photomultiplier tube (PMT) and the magnitude of the PMT signal is proportional to the amount of ozone in the chamber provided there is excess of ethylene as will be shown later. The spectral intensity of the chemiluminescence peaks at about 430 nm (Finlayson *et al.*, 1972). In a similar way to Gregory *et al.* (1983a), we have modified a commercial chemiluminescent ozone instrument (Monitor Labs Inc., Model 8410). The PMT used is Hamamatsu R-268, which has a maximum sensitivity at 420 nm. The schematic diagram of the modified instrument is shown in Figure 1. The major modifications are as follows.

1) Regulation of the ethylene flow by a mass flow controller (STEC, SEC-421 MKII).

2) Regulation of the sum of the sample and ethylene mass flow rates by a combination of a mass flow sensor (Ueshima-Brooks, Type 5810) and a servo controlled needle valve (Ueshima-Brooks, Type 5835).

3) Adoption of an AC driven pump with pumping capability sufficient to enable measurements down to 250 mb with a power consump-

tion of about 30 watts (Nitoh Koki Co., VP0660).

In order to remove aerosols in the sample air with diameters larger than $0.3 \mu\text{m}$, a Teflon (TFE) filter (Sumitomo Electric, AF07P) is mounted at the inlet. Teflon (PFA) tubes with internal diameters of 4.4 and 1.6 mm have been used for plumbing the instrument and for various laboratory tests described below.

3. Laboratory tests

The reaction mechanism for the chemiluminescence is as follows,

where k_i represents the respective reaction rate coefficient and M stands for any molecule. The total emission rate in the reaction chamber can be expressed as follows (O'Brien *et al.*, 1983; Gregory *et al.*, 1983b).

$$I = \frac{k_1}{k_1 + k_2} \frac{k_3}{k_3 + k_4[M]} f_s X \times \left\{ 1 - \exp \left(- \frac{(k_1 + k_2) A (1 - A) [M]^2 V}{f_s} \right) \right\} \quad (1)$$

where

$$A = \frac{[\text{C}_2\text{H}_4]}{[M]} = \frac{[\text{C}_2\text{H}_4]}{[\text{Air}] + [\text{C}_2\text{H}_4]}.$$

f_s (molecules s^{-1}), X , and V (cm^{-3}) denote the mass flow rate of the sample air, ozone mixing ratio, and the volume of the reaction chamber respectively. The brackets denote the concentration of the assigned species in the reaction chamber. For our instrument $V = 16.1 \text{ cm}^3$. The reaction rate coefficients are reported as $k_1 + k_2 = 1.9 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$ (Japar *et al.*, 1974), $k_1 = 3.8 \times 10^{-27} \text{ cm}^3 \text{ s}^{-1}$ (O'Brien *et al.*, 1983), and $k_4/k_3 = 2.8 \times 10^{20} \text{ cm}^{-3}$ (O'Brien *et al.*, 1983). Equation (1) gives the dependence of the emission rate on the sample and ethylene flow rates, temperature, and pressure ($[M]$). It should also

Fig. 1. Schematic diagram of the chemiluminescent ozone instrument. Flow elements are designated as MFC (mass flow controller) and MFM (mass flow meter).

be noted that if these factors are kept constant, I is proportional to ozone mixing ratio. The output signal from the PMT is given by

$$S = C(f_s, f_e, P)I \quad (2)$$

where f_e and P are the ethylene mass flow rate and the pressure in the reaction chamber respectively. Here C is a factor depending on the sensitivity of the PMT and the spatial distribution of the emission in the chamber. As the light gathering efficiency of the PMT decreases with the distance the PMT is from the emitting region, C can be considered to be a function of f_s , f_e , and P . Laboratory tests of the response of the instrument to these parameters should provide the necessary information to understand the physical and chemical characteristics of the instrument.

i) Flow rate dependence

A calculation using the rate coefficients already cited shows that for sample mass flow rates between 100 and 500 STP cm³/min and for ethylene mass flow rates larger than 20 STP cm³/min, the exponential term in equation (1) is much smaller than unity. Here it should be noted that f_s given in the unit of STP cm³/min needs to be converted to that in the unit of molecules s⁻¹ in calculating I from equation (1). Under these conditions, equation (1) can be simplified, to a good approximation, as follows

$$I = \frac{k_1}{k_1 + k_2} \frac{k_3}{k_3 + k_4[M]} f_s X. \quad (3)$$

I increases linearly with f_s and does not depend on the ethylene mass flow rate. The dependence of the chemiluminescent signal S on the sample and ethylene mass flow rates has been measured for a constant ozone mixing ratio of 118 ppbv at 1 atmosphere and is shown in Figures 2(a) and (b) respectively. Throughout the laboratory tests, a UV ozone photometer equipped with an internal UV ozone generator (Thermo Electron Cor., Model 49-100/103) was used to generate ozone from air passed through a charcoal filter and dried with silica gel. The detection limit of the UV photometer is about 2 ppbv. It can be seen from Figure 2(a) that S increases markedly with the sample flow rate. However the rate of increase is not linear, different from the linear in-

Fig. 2(a). Measured output signal of the ozone instrument as a function of the sample mass flow rate for various rates of the ethylene mass flow.

Fig. 2(b). Measured output signal of the instrument as a function of the ethylene mass flow rate for various rates of the sample mass flow.

crease of I expected from equation (3). In addition, as can be seen in Figure 2(b), S increases slowly with ethylene mass flow rate, the largest rate of change in S occurring at small ethylene

mass flow rates. This is again unexpected from equation (3), which indicates that I is independent of the ethylene mass flow rate.

There are two possible causes for these discrepancies. First, the reaction rate coefficient $k_1 + k_2$ used is too large to make the approximation in (3) valid. Second, the factor C in equation (2) is affected by the change in the distribution of the emission in the reaction chamber depending on the flow conditions.

With an increase in the ethylene mass flow rate, the effective emitting region, the volume of which is smaller than that of the reaction chamber, will be closer to the PMT. This will lead to an augmented light gathering efficiency and thus to an increase in the output signal S . Calculations of I reducing $k_1 + k_2$ down by a factor of 10 in maximum have shown that the measured dependence of S on the sample and ethylene mass flow rates cannot be well expressed by the exponential term in equation (1). It is therefore likely that it is the dependence of C on the flow conditions that is causing the corresponding change in the output signal S .

In actually deriving ozone mixing ratios from recorded S values during observations, calibration curves of the ozone mixing ratio versus S are used. They can be given, through laboratory experiments, as functions of f_s , f_e , and P , as is mentioned later. In any case, the ethylene flow as well as the sample flow must be controlled with precision in order to keep constant the sensitivity of the instrument.

ii) Linearity test

If f_s , f_e , and P are kept constant, $C(f_s, f_e, P)$ should be unchanged and therefore, the output signal S is also expected to be linear with ozone mixing ratio (equations (1) and (2)). The value of S as a function of ozone mixing ratio for some combinations of sample and ethylene flow rates have been measured at 1 atmosphere. As an example, the result of the linearity test for the sample and ethylene mass flow rates of 204 and 116 STP cm³/min respectively, is shown in Figure 3. From now on in the explanation of this experiment, the value of the sample and the ethylene mass flow rates in the units of STP cm³/min will be written in abbreviated form which, using the above cases as an example, would be (204, 116). The result for (298, 31) is also given

Fig. 3. Output signal of the instrument versus ozone mixing ratio. The value of the sample (f_s) and the ethylene (f_e) mass flow rates in the units of STP cm³/min is given in abbreviated form as (f_s, f_e). The results obtained one week later are shown as open circles.

in this figure. The standard deviation of the whole data set from the best least square fit is 0.9 ppbv. In this way, the response of S to the ozone mixing ratio has been demonstrated to be linear to within the error of the UV photometer. For the case of (204, 116), the results obtained one week later are shown as open circles to demonstrate the good reproducibility of the system. The stability of the sensitivity was tested further as will be discussed later.

iii) Pressure test

The schematic diagram of the system for the pressure test is shown in Figure 4. The pressure of the sample air is controlled with a servo-controlled needle valve in combination with a calibrated pressure transducer (MKS Baratron). The needle valve is made of stainless steel. The loss of ozone in this valve after it is conditioned with air which contains 200 ± 100 ppbv ozone, has been measured to be 4 to 5% at a pressure of 1000 mb. Prior to detailed tests, the sample

Fig. 4. A laboratory system to test the pressure dependence of the instrument sensitivity. The pressure transducer is designated as P.

mass flow rate f_s , which is not monitored for normal operation, was checked with a calibrated mass flow meter (Tylan, FM360) over the pressure range of the tests. f_s was found to increase by about 3% with a decrease in pressure from 1000 to 400 mb. This was found to be due to the underestimation of the mass flow rate at lower pressures by the sensor used to monitor the total flow rate (Figure 1). This effect does not cause any additional errors in the measurement as the instrument sensitivity is calibrated under these same conditions. In this experiment, the ozone mixing ratio was kept at about 300 ppbv. The ratio of the sensitivity measured at pressures lower than 1 atmosphere to that measured at 1013 mb for five sets of flow rates is shown in Figure 5. The sensitivity at 1000 mb changed by less than 2% through the experiment suggesting an insignificant error caused by the possible change of the ozone loss rate in the needle valve. As can be seen in this figure, the rate of change in the sensitivity down to 600 mb

Fig. 5. Relative sensitivity versus pressure normalized at 1013 mb for various combinations of the sample and ethylene mass flow rates.

is small. In the case of (193, 127), the decrease in the sensitivity is about 5% and 10% at 500 and 400 mb respectively. For larger sample flow rates, the sensitivity changes more rapidly. By contrast, with an increase in the ethylene flow rate, the decrease in the sensitivity at low pressures tends to be reduced. For use in aircraft, it would be desirable to operate the instrument with conditions which require a minimum of corrections. The sample flow rate, which partly defines the response of the instrument, and the operational limitation of the ethylene consumption further limit the choice of the sample and ethylene flow rates. We have chosen the flow rates of (193, 127) as optimum values for aircraft observations.

iv) The effect of interference

In the tests that have been discussed so far, the air used was passed through charcoal and silica gel filters as noted above. The volume mixing ratio of the water vapor of the filtered air was monitored to be lower than 1%, typically about 0.7%. The sensitivity of the chemiluminescent instrument has also been measured by using bottled purified air with a water vapor concentration less than 5 ppmv. For ozone mixing ratios between 70 and 160 ppbv, there was no detectable change in the sensitivity when bottled purified air, filtered air, and ambient air with a water vapor mixing ratio of about 1% were sampled.

It is of interest to further check any possible interferences and the long term stability of the instrument when ambient air is sampled. The chemiluminescent instrument calibrated with the UV photometer, was operated for 6 days in December 1986 sampling outside air together with the UV photometer. The flow condition was chosen to be (298, 31). The zero levels of the two instruments were checked repeatedly with bottled purified air. The zero level of the chemiluminescent instrument was found to be stable to within 0.3 ppbv, while that of the UV photometer occasionally shifted by -5 ppbv rather suddenly. Ozone mixing ratios recorded by the two instruments are compared in Figure 6. The volume mixing ratio of water vapor encountered during this period was between 0.8 and 1.9%. In this figure the data with H₂O mixing ratios between 0.8 and 1.0%, and those with mixing ratios between 1.0 and 1.9% are

Fig. 6. Comparison of the ozone mixing ratio of the outside air measured with the chemiluminescent instrument and by the UV photometer. Open circles are for the data where the H_2O mixing ratio was between 0.8 and 1.0% and the closed circles are for those data where the H_2O mixing ratio was between 1.0 and 1.9%. The straight line is the linear least square fit for the whole data and the dashed line denotes the $X=Y$ relation.

depicted as open and closed circles respectively. The least square linear fit to the whole data set is given by

$$Y = 1.02X + 0.16 \text{ (ppbv)}$$

where X and Y denote the ozone mixing ratio in ppbv obtained by UV and chemiluminescent methods respectively. The standard deviation of the whole data from the best least square fit is 0.90 ppbv. Considering that the detection limit of the UV photometer is about 2 ppbv, it can be said that there is no detectable interference by water vapor for concentrations between 0.8 and 2%. In addition, these results assure us of the long term stability of the chemiluminescent instrument.

4. Precision of the measurement

As far as the present work is concerned, the calibration of the absolute sensitivity depends entirely on the commercial UV photometer, of which the sensitivity is factory set. The UV photometer used for the present experiment has been intercompared with another commercial

UV photometer (Dasibi, Model 1003 AH) of which the sensitivity has also been factory set against a standard instrument. The two UV photometers agreed to within 3% for ozone concentrations between 50 and 150 ppbv. This would give a measure for the absolute accuracy of the calibration of the chemiluminescent instrument. To further improve the accuracy, the photometer and the chemiluminescent instrument need to be calibrated by intercomparison with more reliable standards or ozone sources. The detection limit is determined by the zero drift and the random fluctuation of the output signal. It is estimated to be about 0.5 ppbv from repeated tests with purified air. At ozone concentrations below 10 ppbv, the chemiluminescent instrument appears to be superior to the UV photometer, whose zero level occasionally drifted by 5 ppbv rather suddenly during the 6 days operation.

The tests described above were performed in the laboratory where the temperature ranged between 15 and 30°C. Under these conditions, the change in the sensitivity with temperature did not exceed 5%.

5. Aircraft observation

Aircraft observations of ozone with the chemiluminescent instrument were made on December 16 and 17, 1985 at latitudes between 28 and 38°N up to an altitude of 6 km. The observations were made mostly over the sea near Japan along the meridian of about 140°E. The instrument was operated at the flow rates of (193, 127) as already noted. The air intake system is described in Kondo *et al.* (1987). The air was sampled through a 3.4 m long Teflon (PFA) tube with an inner diameter of 4.4 mm. The total volume of the sample tube and the reaction chamber was 68 cm³. The residence time of the sample air in this volume is about 20 and 10 s at the pressures of 1000 and 500 mb respectively. The temperature of the sample air was monitored to be between 10 and 30°C, depending on the temperature in the cabin of the aircraft. It has been found from laboratory tests that the output signal of the instrument becomes stable 10 minutes after it has been powered up. The output signal for ozone was digitized by a 12-bit AD converter and recorded every 10 s with a micro-

Fig. 7(a). Measured ozone mixing ratio on board the aircraft on December 16, 1985 at latitudes between 33 and 34°N.

Fig. 7(b). Same as for Fig. 7(a) but for the latitudes between 28 and 33°N.

computer. The measured ozone concentration together with the temperature is shown in Figures 7(a), (b), and (c). The short term fluctuations of the total and ethylene mass flow rates did not exceed 2% and the drift of the total mass flow rate was about 2% throughout the observa-

Fig. 7(c). Same as for Fig. 7(a) but for December 17, 1985 and the latitudes between 35 and 38°N.

tional series. It can be seen from these figures that the measured ozone mixing ratio in the mid-troposphere is in the range between 40 and 60 ppbv with a number of small scale structures. Further analysis of this data, together with that of NO_x which was measured simultaneously, will be reported elsewhere.

6. Summary

A chemiluminescent instrument for ground-based observations of ozone was modified for aircraft observations. A series of detailed test showed that the sample and ethylene mass flow rates need to be controlled precisely in order to maintain constant sensitivity both for ground-based and aircraft observations. The sensitivity changes little between 1000 and 500 mb and the reduction of the sensitivity at pressures lower than 400 mb can be minimized by selecting optimum sample and ethylene flow rates.

The dependence of the output signal on the sample and ethylene flow rates and on the pressure is not identical to that of the calculated total emission rate. This suggests that the spatial

distribution of the photo-emission in the chamber changes considerably depending on the flow conditions. This is due in part to the slow reaction rate of ethylene and ozone. It is therefore likely that the present design of the chamber is not necessarily the best suited for aircraft observations.

No serious interference from water vapor has been detected. It seems that the chemiluminescent instrument can be more accurate than UV photometers, especially at low ozone mixing ratios. This is mainly due to the relative stability of the zero level and the high signal to noise ratio. In addition, the short "warm up" time required is suited to aircraft observations.

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航空機観測のための化学蛍光法オゾン測定器

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エチレン-オゾンの化学蛍光法によるオゾン測定器を改修して、サンプル空気及びエチレンの流量を外気圧に無関係に一定に保てるようにした。

この測定器の特性を実験室で詳しく試験した結果以下の事が判明した。

- (1) 測定器の感度はサンプル大気の流れにより大きく変わる。
- (2) エチレン質量流量に対する感度依存性はこれに比べかなり小さい。
- (3) ゼロレベル及び直線性からのずれから生じる測定誤差は1 ppbv より小さい。
- (4) 1000から500 mbの間での感度の変化は小さいが、500 mb以下では測定した校正値に基づく補正が必要となる。その補正は400 mbでは約10%である。

この測定器を用いて高度6 kmまでのオゾンの航空機観測を行った。このとき流量制御系は流量を3%の精度で一定に保った。この観測で得られたオゾン濃度も報告する。