A NOTE ON THE NEW TYPE HYGROMETER USING THE PHOTOCHEMICAL REACTION:
$H_2O+h\nu$(Ly-α line)$\to$OH*+H, and OH*$\to$OH+$h\nu$ (λ=309 nm)

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Abstract: The fluorescence effect of OH*, and the attenuation effect of the Ly-α light source intensity due to the photochemical reactions, $H_2O+h\nu$ (λ=121.6 nm, Ly-α line)$\to$OH*+H, and OH*$\to$OH+$h\nu$ (λ=309 nm) are useful for measuring the atmospheric water vapor content. A prototype hygrometer was built applying these effects, and the procedure for data reduction was confirmed. We examined the feasibility of this data reduction method in the practical airbone use of the instrument in the troposphere. The results confirm the instrument can be used to measure the water vapor content not only in the stratosphere but also in the troposphere.

1. Introduction

Though the stratosphere and the mesosphere are particularly dry atmospheric regions, it is very important from several aspects to measure accurately the distribution of water vapor, H_2O. On one hand, water vapor can be used in the lower stratosphere as a tracer of the air-exchange process between the troposphere and stratosphere, and of the global air circulation. On the other hand, H_2O participates in various photochemical reactions in the upper atmosphere.

The photochemical reactions shown in eq. (1) have been considered to be very useful for measuring the water vapor content in a dry atmosphere such as the upper atmosphere,

$$H_2O+h\nu(\lambda=121.6 \text{ nm, Ly-}\alpha \text{ line})\to OH(A^2\Sigma^+)+H ,\tag{1a}$$

$$OH(A^2\Sigma^+)+M(M=O_2 \text{ or } N_2)\to\text{products} ,\tag{1b}$$

$$OH(A^2\Sigma^+)\to OH(X^2\Pi)+h\nu(\lambda=309 \text{ nm}) .\tag{1c}$$
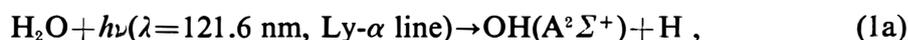
The reactions (1b) and (1c) proceed so rapidly that it can be assumed that the concentration of the excited state OH radical is chemically in equilibrium with H_2O vapor concentration. Therefore the intensity of fluorescence light in reaction (1c) per unit volume, *I*, can be expressed by the following equation under the assumption that the

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reaction (1b) dominates in the decay of the OH radical (IWASAKA *et al.*, 1981),

$$I=\frac{JeA}{k_{air}}\mu ,$$ (2)

where

J   :   the photodissociation constant of the reaction (1a),
e   :   the quantum yield of the reaction (1a),
A   :   the transition probability of the reaction (1c),
k_{air} :   the quenching rate constant of air molecules of the reaction (1b),
μ :   the volume mixing ratio of water vapor.

The volume mixing ratio of water vapor in the atmosphere can be obtained by measuring the fluorescence light intensity.   During the past few years some investigators have measured the water vapor content in the stratosphere by applying this method (KLEY and STONE, 1978; BERTAUX and DELANNOY, 1978; KLEY *et al.*, 1979).

IWASAKA *et al.* (1981) have developed a prototype hygrometer which applies the photochemical reactions mentioned above (we call this hygrometer the Ly-α/OH fluorescence hygrometer), and on the basis of laboratory experiments have suggested that this method is a very promising one for measuring the water vapor content in a very dry atmosphere.   In the consequent experiments we applied a more accurate data reduction method than the previous one consequently succeeded in extending the measurable range up to several thousand ppmV.   We have tried to measure the water vapor content using an airborne version of this instrument in order to check following points:

   1)   Usefulness of chemical reaction (1c) to measure the water vapor content in dry atmospheric condition (usually expected above about 5 km altitude).

   2)   Reexamination of data reduction procedures.

   In this paper we will first explain the method of data reduction, and then we will present the preliminary results of the airborne use of this instrument.

2.   Method of Data Reduction

As shown in the previous paper (IWASAKA *et al.*, 1981), the output of the photon counter of this hygrometer is proportional to the volume mixing ratio of water vapor and also is dependent upon the decrease of the light source intensity (Ly-α light) through the absorption by water vapor molecules and oxygen molecules.   There will be appreciable flux due to extraneous lights from the hydrogen lamp.   These relations can be in the following equations:

$$I_p=C_1F_0X\mu+C_2F_0$$ (3a)

$$X=\int_a^b \exp(-\tau x)\mathrm{d}x$$

$$=[\exp(-\tau a)-\exp(-\tau b)]/\tau$$ (3b)

$$\tau=\sigma_{O_2}[O_2]+\sigma_{H_2O}[H_2O] ,$$ (3c)

where

I_p: the counting rate of the photon counter,

F_0:   the photon flux of Ly-α light source,

$\sigma_{O_2}, \sigma_{H_2O}$:   the absorption cross section of oxygen and water vapor molecules at a wavelength of 121.6 nm,

$[O_2], [H_2O]$:   the number density of oxygen and water vapor molecules in the air,

C_1, C_2:   constants accounting for geometrical effects and physical parameters such as the reaction rate constant or quenching rate constant,

a, b: lengths which determine the viewing area of the photomultiplier (see Fig. 1).

Equation (3) explains well the relation between the output of the photon counter and the volume mixing ratio of water vapor as shown in Fig. 2. The nonlinearity of the curve for the absorption of Ly-α light due to oxygen and water vapor molecules is noted. This effect is expressed by the term X in eq. (3b) in order to deduce the volume mixing ratio of water vapor from the output of the instrument, we rewrite eq. (3a) as follows:

$$\mu = (I_p - C_2 F_0)/(C_1 F_0 X) .$$ (4)

The value of $C_2 F_0$ can be estimated by extrapolating the calibration curve to the point $\mu = 0$. The output of the NO-ion chamber facing the hydrogen lamp (see Fig. 1) corresponds to the transmittance of the air along the sensing path. The magnitude of X can be deduced from this output. The value of $C_1 F_0$ can be also determined from
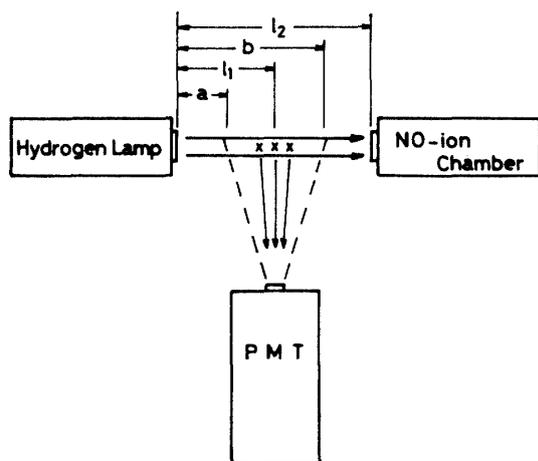
Fig. 1.   Schema of the principle of the instrument.
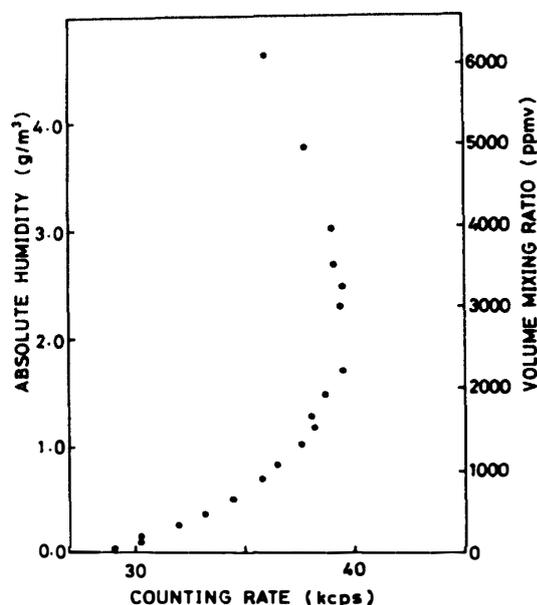
Fig. 2.   Output counting rate of the photon counter versus water vapor in the air (IWASAKA et al., 1981). Calibration curves can be varied by using various arrangements of individual components in the sensing unit.

the calibration curve. Kley and Stone (1978) and Kley *et al.* (1979) presented a simple way to deduce the mixing ratio of water vapor. In their research the Ly-α light intensity at the center of the viewing area of the photomultiplier was considered to be the suitable value for estimating X. The factor corresponding to X in their work was as follows:

$$X=(b-a)\exp(-\tau l_1),\tag{5a}$$

$$l_1=(a+b)/2.\tag{5b}$$

To obtain the value of μ they divided the value $I_p-C_2F_0$ by the output of the second NO-ion chamber which produced the value $F_0\exp(-\tau l_1)$ (Kley *et al.*, 1979). However, this method does not always give correct values of for the following reasons. Firstly, the logarithmically amplified output of the NO-ion chamber used here seems to be not a linear but an exponential function of τl_1. Therefore it is doubtful that the direct output of the NO-ion chamber is proportional to $F_0\exp(-\tau l_1)$. Secondly, the approximation of X using eq. (5) causes some error in data reduction owing to neglect of the so-called "pre-absorption" over the viewing area of the photomultiplier. Figure 3 is an example of the variation of X with altitude for various water vapor mixing ratios. The curves indicated by solid lines are accurate expressions of X from eq. (3b), and those by broken lines are approximate expressions of X from eq. (5a). In the upper atmosphere (very dry atmosphere), the difference between two expressions is small, less than a few percent. However, if one desired to extend the measuring
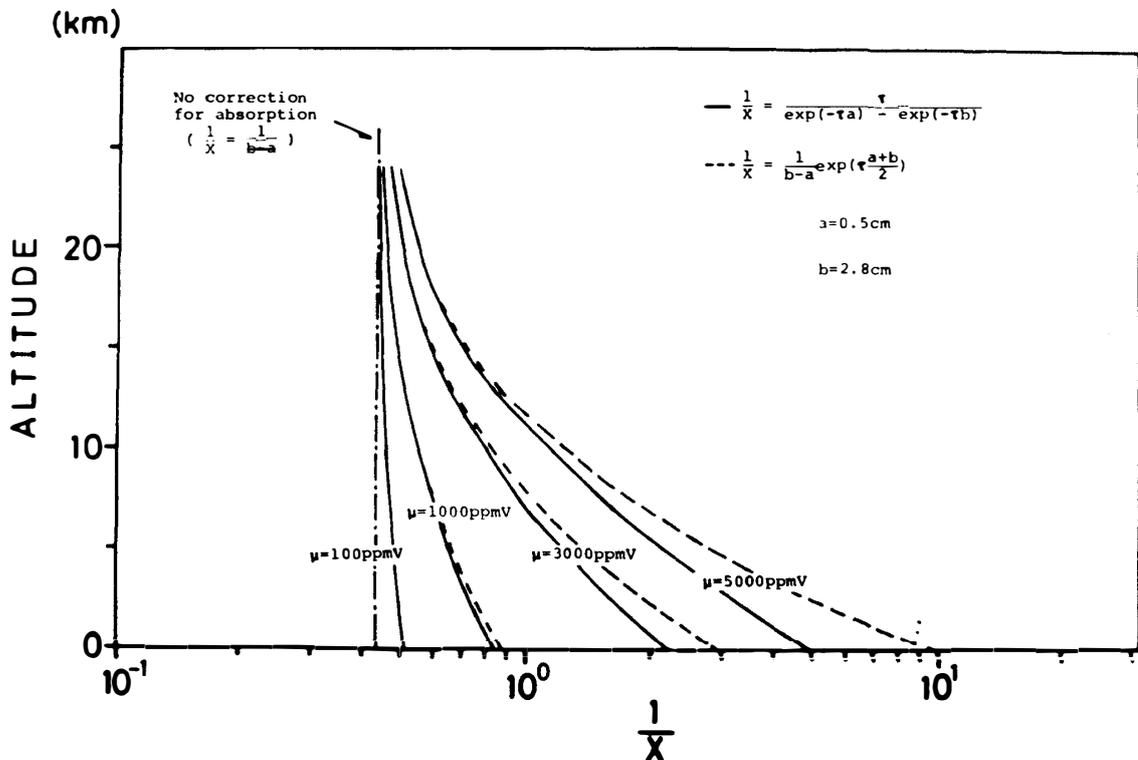
Fig. 3. The values of $1/X$ in eq. (4) versus altitude for various volume mixing ratios of water vapor. The number density of air molecules is based upon the model atmosphere (US Standard Atmosphere, 1976).

range of water vapor content to several thousand ppmV, as is found frequently in the troposphere, the discrepancies would become more than about 30%. Therefore, it is better to obtain the relation between the value of τ and the output of the NO-ion chamber empirically. Then the strict calculation of X using eq. (3b), even if it is a little complicated, should be adopted in deducing the volume mixing ratio of water vapor from the output of the photon counter. Figure 4 shows an example of the calibration of our prototype Ly-α/OH fluorescence hygrometer. The two ways of data reduction mentioned above were applied. The accurately corrected counting rates correspond linearly to the volume mixing ratio of water vapor even beyond the value of 5000 ppmV. On the other hand, the plot for the approximately corrected counting rates is not linear. The magnitude of the indicated in Fig. 4 increases as the volume mixing ratio of water vapor increases because of the dependence of the correction factor $1/X$ upon water vapor content in the air as shown in Fig. 3. This kind of error which is due to thermal noise of the photomultiplier can be easily eliminated with the use of a lawpass filter such one whose cut-off frequency is 0.2 Hz.
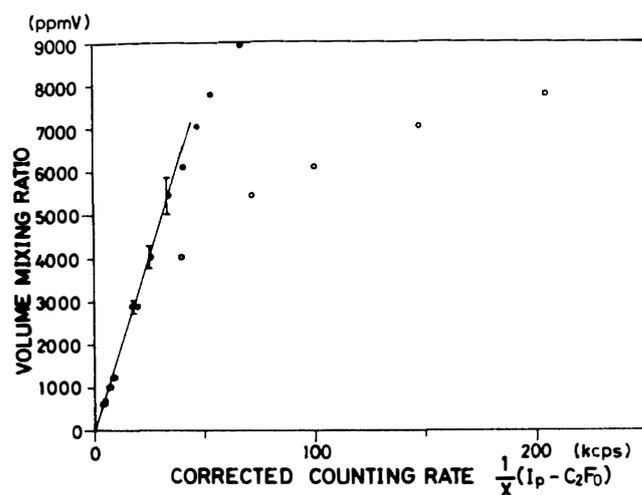
Fig. 4. *Corrected counting rate versus the volume mixing ratio of water vapor. The filled circles give the correction based upon eq. (3b), and the open circles the correction based upon eq. (5a). The I on the fitting line indicates the error range corresponding to an error of ± 0.5 kcps in the value of original counting rate I_p.*

3. Preliminary Results of the Airborn Use of the Instruments

Although the final goal of our work is to measure the water vapor content accurately in the middle atmosphere, especially, in the polar middle atmosphere, the results shown in Fig. 4 encourage us to use the Ly-α/OH fluorescence hygrometer in wide range of water vapor mixing ratios. In addition to the laboratory experiments, we should like to present recent results of aircraft measurements in order to confirm the feasibility of the data reduction method presented here. On June 24, 1981 we tried to make aircraft measurements of water vapor content in the troposphere (from near the ground up to 5 km height) using the prototype Ly-α/OH fluorescence hygrometer. The sampled air was continuously introduced at the nose of the aircraft (Cessna 402)
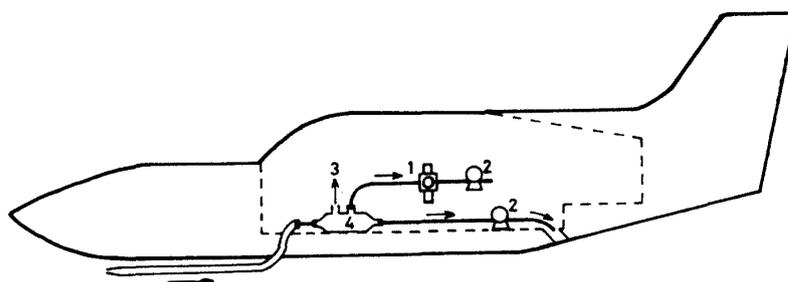
Fig. 5.   *Schematic representation of the method of air sampling in the aircraft observation.*
1. Sensing unit of the instrument, 2. Pump, 3. Air sample opening for other research,
4. Air sample chamber, → Air flow.
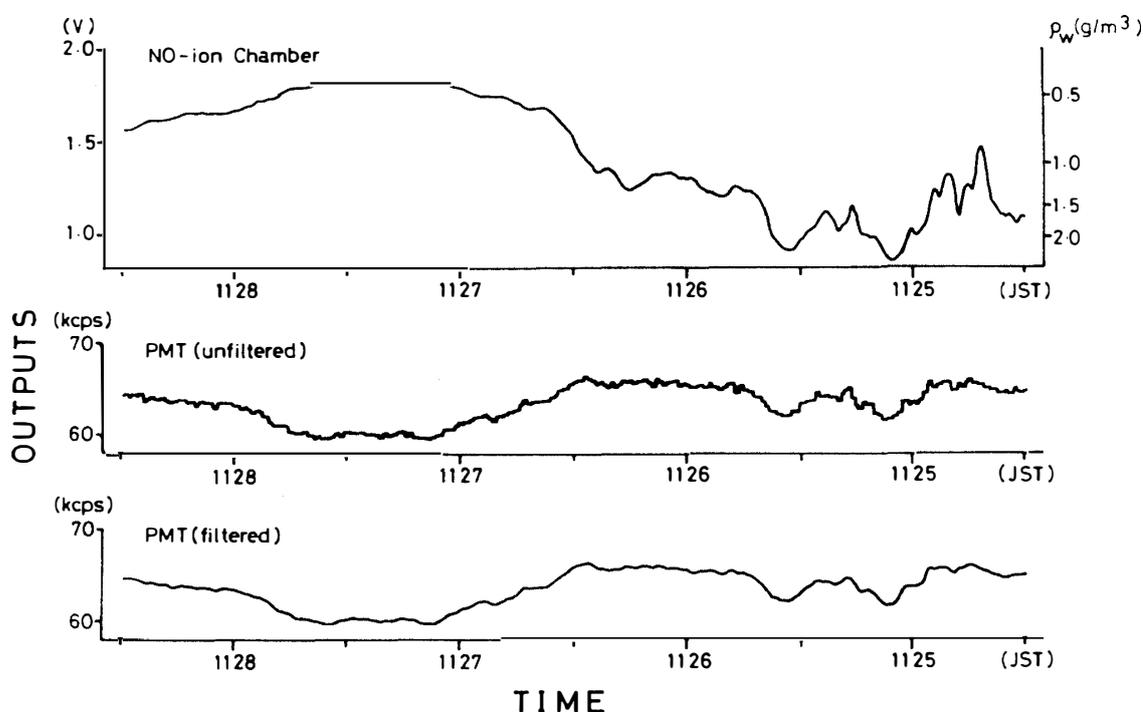
Fig. 6.   *Typical output of the instrument for the aircraft observations (June 24, 1981, over Mikawa district). The upper panel shows logarithmically amplified output of the NO-ion chamber. Right ordinate indicates absolute humidity. The middle panel shows direct output of the photon counter. The left ordinate indicates counting rates. The lower panel shows outputs of the photon counter smoothed by a lowpass filter whose cut-off frequency is 0.2 Hz.*

through a air-sampling tube set along the fuselage, with the aid of pumps, into the sensing unit of the instrument (see Fig. 5).

As can be seen from Fig. 4, the instrument can measure the volume mixing ratio of water vapor in the range less than 6000 ppmV. These conditions are relatively dry ones as found in the summer lower troposphere. Fortunately, however, we encountered these conditions in our observations. Figure 6 is an example of direct outputs of the instrument obtained during a level flight at a height of 4 km. The upper panel shows logarithmically amplified outputs of the NO-ion chamber, in which drier air conditions correspond to higher output voltage. The middle panel shows
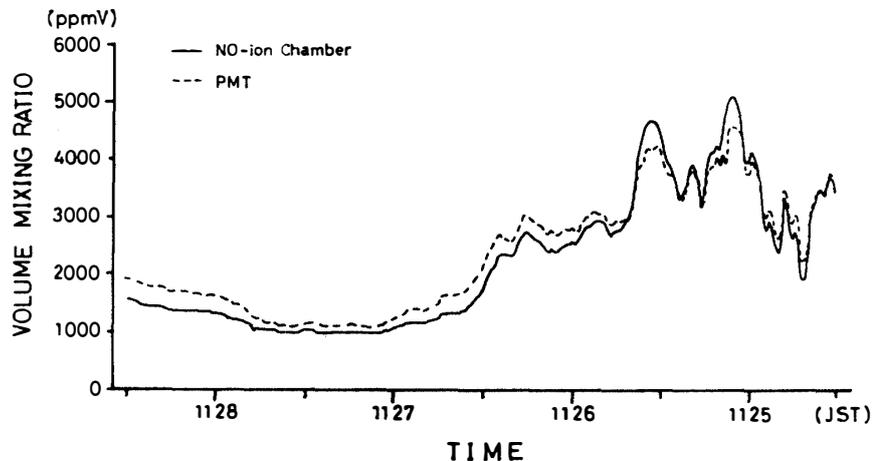
Fig. 7.   The results of conversion of the data shown in Fig. 6 into the volume mixing ratio of water
vapor.   The accurate data reduction method described in the Section 2 was applied to obtain
the results shown by the broken line.   The results shown by the solid line were deduced from
the absolute humidity obtained with the NO-ion chamber using the air density values of the
US Standard Atmosphere, 1976.

direct outputs of the photon counter.   Small fluctuations in the counting rates can
be seen, which would be due to thermal noise associated with photon counting methods.
We eliminated these fluctuations with the aid of a lowpass filter whose cut-off frequency
was 0.2 Hz.   The results are shown in the lower panel.   The outputs of the photon
counter showed the nonlinear feature seen in Fig. 2.   The decrease of counting rates
around 1125 JST corresponded to moister air conditions, whereas that around 1127
JST corresponded to drier air conditions.   However, we can deduced the volume
mixing ratio of water vapor from outputs of the NO-ion chamber and the filtered
outputs of the photon counter according to the method described in the Section 2.
The results are shown by the broken line in Fig. 7.   The solid line in this figure indicates
the volume mixing ratio of water vapor obtained in another way: first converting the
outputs of the NO-ion chamber into absolute humidity, and then dividing them by
the dry air density (we used the table of air density in US Standard Atmosphere,
1976 in this study).   The combination of a hydrogen lamp and a NO-ion chamber,
utilizing the attenuation of the Ly-α light through an air sample, and its output,
corresponding to absolute humidity, will be reliable in the humidity range of Fig. 7.
Comparing two curves, we see a discrepancy between two methods in the absolute
values differing as much as 10%.   This can be attributed to the fact that true air density
was not measured in the observation, and that it was difficult to obtain a precise value
of C_2F_0 for eq. (4) (the procedure of calibration is a liltte crude at present).   However,
the time variations of the two curves were almost identical, which confirms the pro-
priety of our data reduction method in field use and demonstrates the rapid response
of the Ly-α/OH fluorescence hygrometer.

Being able to extend the measurable range of our new hygrometer, in favorable
conditions we will be able to measure the volume mixing ratio of water vapor from the
ground to the middle atmosphere with only one instrument using the same data re-
duction method, not requiring other sensors for temperature and pressure.

4. Summary

Summarizing the present experiment with the new type hygrometer using photo-chemical reductions of water vapor, we can conclude that the procedure for data reduction was satisfactory. In addition, it is suggested that this hygrometer is useful for measuring the water vapor content not only in very a dry atmosphere such as the middle atmosphere but also in the troposphere.

Acknowledgments

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