Development of an Analytical System Based on a Magneto-pneumatic Oxygen Analyzer for Atmospheric Oxygen Determination

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A high-precision analytical system to observe the variations in the amount fractions of atmospheric oxygen with a very small uncertainty was developed. The system comprises a magneto-pneumatic oxygen analyzer and three automatic pressure controllers. The drift of the analyzer’s signal intensity can be reduced when the amount fractions of oxygen in the sample and reference gases are similar because the temperature coefficient of the analyzer linearly depends on the difference between these amount fractions. The repeatability of oxygen determination and the long-term stability of the system were tested to assess the applicability of the analyzer to field-based measurements for continuous atmospheric observations. The standard deviation of the average for 10-min measurements in the 5-day long-term stability test was 0.7 μmol mol⁻¹ after a temperature correction. This indicates that the system can continuously measure the amount fractions of oxygen in the atmosphere for a few days without interruption for any calibration and/or compensation for the signal drift.

Keywords Paramagnetic oxygen analyzer, magneto-pneumatic oxygen analyzer, oxygen standard gas, uncertainty, high precision, temperature coefficient, atmosphere observation

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Introduction

An accurate estimation of the flux of carbon dioxide between the atmosphere, the ocean, and the terrestrial biosphere is difficult. Therefore, measuring atmospheric oxygen levels is a useful approach to study the carbon cycle.¹⁻⁵ The World Meteorological Organization (WMO) recommends that the uncertainty is less than 2 per meg when monitoring oxygen; this value corresponds to an amount fraction of oxygen of 0.4 μmol mol⁻¹.⁶ The unit per meg is defined as

$$\delta(O_2/N_2)(\text{per meg}) = \frac{(O_2/N_2)_{\text{sample}} - (O_2/N_2)_{\text{reference}}}{(O_2/N_2)_{\text{reference}}} \times 10^6,$$  (1)

where $(O_2/N_2)_{\text{sample}}$ and $(O_2/N_2)_{\text{reference}}$ are the ratios of oxygen to nitrogen amount fractions in the sample and reference, respectively. Analytical systems to measure the amount fractions of atmospheric oxygen within an uncertainty of a few per meg or less have been previously developed; these systems are based on different principles, such as interferometry, mass spectrometry, paramagnetic analysis, vacuum ultraviolet absorption spectrometry, gas chromatography, and fuel cells with pressure references and differential pressure controllers.¹⁻¹² Oxygen analyzers based on such principles may have advantages (small size and power consumption, good stability and repeatability, and continuous measurements or high time resolution) as well as disadvantages (large size and power consumption, requirement of frequent calibration, and batch sampling). Therefore, we have attempted to develop an oxygen analyzer based on a different principle.

When the amount fraction of oxygen in a previously developed certified reference material (NMIJ CRM 3404-c) was determined, the drift of a magneto-pneumatic oxygen analyzer was quite small.¹³ The magneto-pneumatic oxygen analyzer is a type of paramagnetic analyzers and is based on the pressure differences caused by the attraction of oxygen molecules to a magnetic field.¹⁴⁻¹⁷ No controllers were used therein to maintain a constant pressure in the sample; however, the drift of the analyzer’s signal in 1 h was within 5 mV, which corresponds to 2.5-μmol mol⁻¹. This indicates that the signal drift of the analyzer can be improved by stabilizing the sample pressure and temperature.

The stability of an oxygen analytical system comprising a magneto-pneumatic oxygen analyzer and automatic pressure controllers was studied herein. We aimed at achieving an uncertainty of 1 μmol mol⁻¹ for the oxygen measurement by maintaining a constant temperature and pressure. Although the sample chamber of the analyzer was wrapped with a heat insulator to maintain the sample chamber temperature constant, the signal intensity drifted due to a change of the room temperature. To reduce the signal drift, the relations between the signal intensity of the analyzer and the temperature of the sample chamber as well as that between sample pressure and noise intensity was investigated herein. In addition, we...
demonstrated that the signal drift of the magneto-pneumatic oxygen analyzer caused by variations in the temperature can be reduced when the amount of oxygen fraction in a reference gas is appropriately adjusted in the analyzer.

For continuous-field-based measurements of the atmospheric oxygen variation, the analyzers should be small and have high precision, low cost, fast response, high time resolution for continuous data acquisition and low power consumption. The analytical system evaluated in this study seems to be appropriate for such measurements; we therefore tested the repeatability and long-term stability of this system to demonstrate its applicability.

To clearly distinguish between the absolute (barometric) and gauge pressures, either “A” or “G” is respectively added after the kPa units, i.e., “kPaA” or “kPaG.”

Experimental

Measurement apparatus

The main component of the oxygen analytical system is the magneto-pneumatic oxygen analyzer. This analyzer was purchased from Air Liquide Japan (Model POM-6E), and it is similar to a model of OXYMAT 6E (SIEMENS, Germany). The analyzer was housed in a 19-inch rack unit with a width, height, and depth of 483, 177, and 495 mm, respectively. Since the rack unit is designed to contain two analyzers, it occupied only half of the unit. According to the manufacturer’s specifications, the lowest measuring range and repeatability of the analyzer are 0.5 cmol mol⁻¹ and 1% of the current measuring range, respectively. From these values, the repeatability is estimated as 50 μmol mol⁻¹. Before conducting all of the measurements, the magneto-pneumatic oxygen analyzer was calibrated using the two-point calibration curve method with standard gases at appropriate amount fractions. The standard gases were prepared using the gravimetric method. The signal output is electric current (0 – 20 mA), which is converted to voltage (0 – 10 V) by a 500-Ω wire-wound resistor (UPW50, TE Connectivity, USA) with a typical temperature coefficient of 3 ppm °C⁻¹. The voltage was measured and transferred to a computer every 4 s using a digital multimeter (R6452A, Advantest, Japan).

Figure 1 schematizes the oxygen analytical system based on the magneto-pneumatic oxygen analyzer. This system was located in an air-conditioned room. Two inlets were provided to the magneto-pneumatic oxygen analyzer: one for the sample gas and the other for the reference gas. The pressures of the sample and reference gases introduced were controlled using automatic pressure controllers (APCs), APC1 and APC3 (UR-Z712M, Horiba STEC, Japan). The sample and reference gases were mixed and exhausted using the outlet; the outlet pressure was controlled using a third APC (APC2) (UR-Z712M-B, Horiba STEC, Japan). The operation of the three APCs was considered to accurately control the pressure of both the gases in the magneto-pneumatic oxygen analyzer. The flow rate of the sample was controlled by the APCs, because pressure loss in the analyzer increases as the flow rate increases; this control can be achieved when the pressures of the APCs are appropriately set. The restrictors shown in Fig. 2 maintain a constant flow rate of the reference gas. The pressure control range of all APCs was 0 – 300 kPaA. The stated accuracy of the APCs is 0.5% of the full scale. The pressure values at the APCs were monitored and logged by a computer via RS-485 communication ports every 4 s.

Standard gas mixtures and samples

The gas mixtures shown in Tables 1 and 2 were prepared from pure oxygen (G1 grade, >99.9999%, Japan Fine Products, Japan) and pure nitrogen (G1 grade, >99.9999%, Japan Fine Products, Japan) using the gravimetric method in accordance with ISO 6142-1:2015. The gas mixtures were introduced into the analyzer as either a sample or a reference gas. The standard uncertainty of the amount fraction of oxygen was 3 μmol mol⁻¹. The 10-L aluminum alloy cylinders were filled with the gas mixtures. Certain standard gas mixtures were adjusted to approximately 1 cmol mol⁻¹ argon by adding pure argon (G1 grade, >99.9999%, Japan Fine Products, Japan) using the gravimetric method. Impurities in the pure oxygen, nitrogen, and argon were analyzed using different techniques: gas
The balance gas is nitrogen. The standard gases listed were used for the evaluation of the temperature dependence.

<table>
<thead>
<tr>
<th>No.</th>
<th>O₂ amount fraction/cmol mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std#1</td>
<td>20.6493</td>
</tr>
<tr>
<td>Std#2</td>
<td>19.5763</td>
</tr>
<tr>
<td>Std#3</td>
<td>19.9437</td>
</tr>
<tr>
<td>Std#4</td>
<td>21.3704</td>
</tr>
<tr>
<td>Std#5</td>
<td>19.8970</td>
</tr>
</tbody>
</table>

The balance gas is nitrogen. The standard gases listed were used for the repeatability of the quantification using the magneto-pneumatic oxygen analyzer.

Table 2 Amount fraction of oxygen in standard gases prepared using the gravimetric method according to ISO 6142-1:2015

<table>
<thead>
<tr>
<th>No.</th>
<th>O₂ amount fraction/cmol mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Std#6</td>
<td>19.7565</td>
</tr>
<tr>
<td>Std#7</td>
<td>19.8026</td>
</tr>
<tr>
<td>Std#8</td>
<td>19.9626</td>
</tr>
</tbody>
</table>

The balance gas is nitrogen. The standard gases listed were used for the evaluation of the temperature dependence.

Results and Discussion

The pressure difference, \( \Delta P \), at the micro-flow sensor (shown in Fig. 2) is induced by the paramagnetism of oxygen; this pressure difference is utilized as the measurement principle of the magneto-pneumatic oxygen analyzer. Sample and reference gases are introduced into the magneto-pneumatic oxygen analyzer; then, the reference gas separates into two flows and enters the sample chamber via the orifices (flow restrictors), as shown in Fig. 2. When the sample gas reaches an inhomogeneous magnetic field, the oxygen molecules in the sample are attracted to the center of the magnetic field owing to their paramagnetism, and the attraction causes a back pressure in the path of the reference gas present at the magnetic field side. The pressure difference between the two paths of the reference gas results in a flow; the flow is detected using the micro-flow sensor.

According to Curie’s law, the paramagnetic susceptibility per unit mass is inversely proportional to the absolute temperature. The paramagnetic susceptibility per unit volume is basically proportional to the absolute pressure of the sample and to the reciprocal of the squared absolute temperature because the densities of the gases are proportional to the absolute temperature. The difference, \( \Delta P \), is proportional to the absolute pressures of the sample gases, the reciprocal of the square of absolute temperature, and the difference in the amount fractions of oxygen between the sample and reference gases. It is expected that the stabilization in the temperature and pressure of the gases in the sample chamber would reduce the signal intensity drift of the magneto-pneumatic oxygen analyzer. The results concerning the drift and variance of the analyzer related to the temperature, pressure, and the difference of amount fractions between the sample and reference gases is presented herein, and the applicability of the analytical system for the measurement of oxygen fractions in the atmosphere is discussed.

Temperature dependence

The sample chamber of the magneto-pneumatic oxygen analyzer was wrapped in polyethylene heat insulators to maintain a constant temperature. A platinum resistance thermometer (R060-33, Chino, Japan) was adhered to the sample chamber to measure the temperature. The sample chamber exhibited an improved signal stability compared to a chamber without insulators; however, the signal intensity of the analyzer still drifted significantly, even though the temperature on the chamber varied by only ±0.1°C. To use the analyzer in-field-based measurements, its stability needs to be improved to make it more tolerable to variations in the temperature.

The temperature dependence of the signal intensity was examined. The pressure of APC1 and APC2 were set to 105.00 and 104.76 kPaA, respectively. The flow rate of the sample gas under these conditions was approximately 100 mL min⁻¹. The full measurement range of the analyzer was set at the smallest possible value (0.5 cmol mol⁻¹ oxygen amount fraction); e.g., from 19.5 to 20 cmol mol⁻¹. A 2-mV difference in the signal intensity corresponds to a 1-μmol mol⁻¹ difference in the amount fraction of oxygen. Before measuring the temperature dependence, the analyzer was calibrated using standard gas mixtures, Std#2 and Std#3, as shown in Table 1. The relation between the temperature and signal intensity when the sample and reference gases were respectively Std#3 and Std#1 is shown in Fig. 3. The error bars in Fig. 3 represent twice the standard deviations; these deviations indicate a 95% confidence interval. The signal intensity linearly increases as the absolute temperature increases, as shown in Fig. 3. The temperature coefficient
The pressure difference, $P_{\Delta}$, of the reference gas at the micro-flow sensor is induced by the magnetic field into the sample chamber. The pressure difference is divided into two flow paths, one passes through the reference gas and the other through the sample gas. This result also supports the assumption that $P_{\Delta}$ does not become zero when the value of $(C - C_k)$ decreases.

The noise intensity of the magneto-pneumatic oxygen analyzer was calibrated using two of the standard gases listed in Table 1 in cases wherein the reference gases changed. As shown in Fig. 4, the temperature coefficients linearly decrease as $(C - C_k)$ decreases. The slope of a regression line fitted to the data using weighted least-squares method corresponds to the dependence of the temperature coefficients on the oxygen fraction difference, or the differential of Eq. (4) in relation to the fraction difference, which is given as

$$S_x' = \frac{dS_x}{d(C - C_k)} = -2a \frac{P}{T^3}.$$  

The value of the slope and its expanded uncertainty $(k = 2)$ are $-0.187$ and $0.003$ V K$^{-1}$ (cmol mol$^{-1}$)$^{-1}$, respectively. The noise intensity of the magneto-pneumatic oxygen analyzer was evaluated using the standard deviation at different sample pressures by changing the forward and back pressures of the sample chamfer using APC1 and APC2. The noise intensity was evaluated from the standard deviation of a discrete measurement in 5 min (75 data points). The results obtained

$$S = a \left( \frac{P(C - C_k - C_0)}{T^2} \right) + b,$$

where $a$ and $b$ are coefficients to be determined from the calibrations of the magneto-pneumatic oxygen analyzer. The temperature coefficient, $S_T$, is obtained by differentiating Eq. (3):

$$S_T = \frac{dS}{dT} = -2a \frac{P(C - C_k - C_0)}{T^3}.$$  

It is expected from Eq. (4) that the temperature coefficient, $S_T$, is linear to the difference in the amount of oxygen between the sample and reference gases. Figure 4 shows the temperature dependence when the fraction difference $(C - C_k)$ changed. The pressures of APC1 and APC2 were set to 105.00 and 104.76 kPaA, respectively. The temperature of the sample chamber was approximately 51°C. The error bars in Fig. 4 represent the expanded uncertainty of the temperature dependence $(k = 2)$. To change the value of $(C - C_k)$, the sample and reference gases were selected from the standard gases in Table 1. The magneto-pneumatic oxygen analyzer was calibrated using two of the standard gases listed in Table 1 in cases wherein the reference gases changed. As shown in Fig. 4, the temperature coefficients linearly decrease as $(C - C_k)$ decreases.

The slope of a regression line fitted to the data using the least-squares method corresponds to the dependence of the temperature coefficients on the oxygen fraction difference, or the differential of Eq. (4) in relation to the fraction difference, which is given as

$$S_x' = \frac{dS_x}{d(C - C_k)} = -2a \frac{P}{T^3}.$$  

The value of the slope and its expanded uncertainty $(k = 2)$ are $-0.187$ and $0.003$ V K$^{-1}$ (cmol mol$^{-1}$)$^{-1}$, respectively. The value of the x-intercept of the regression line $C_k$ and its expanded uncertainty $U(C_k)$ $(k = 2)$ are 0.192 and 0.013 cmol mol$^{-1}$. This indicates that the signal intensity is less affected by the temperature drift when the difference of oxygen fractions between the sample and reference gases is 0.192 cmol mol$^{-1}$. This result also supports the assumption that $P_{\Delta}$ at the sensor does not become zero when the value of $C$ is similar to $C_k$.  

**Pressure dependence**

As the sample pressure increases, the signal intensity of the analyzer increases, and the signal-to-noise ratio is expected to decrease. The noise intensity of the magneto-pneumatic oxygen analyzer was evaluated using the standard deviation at different sample pressures by changing the forward and back pressures of the sample chamber using APC1 and APC2. The noise intensity was evaluated from the standard deviation of a discrete measurement in 5 min (75 data points). The results obtained
when the pressure at APC1 varied from 105 – 280 kPaA are shown in Fig. 5. The error bars in Fig. 5 represent twice the standard deviation. The pressure of the reference gas was set to
300 kPaA, and the set values of APC1 were approximately
0.1 kPa higher than those of APC2. Under these conditions, the flow rate of the sample gas was 100 mL min⁻¹. The flow rate of the reference gas decreased as the pressure of the sample gas increased; the rate was 5 mL min⁻¹ when the pressure of the sample was 180 kPaA. The two-point calibrations of the magneto-pneumatic oxygen analyzer were performed whenever the sample pressure changed.

As the pressure of the sample gas increased, the noise intensity decreased and was almost constant when the sample gas pressures were higher than 180 kPaA. The standard deviation at 180 kPaA is 1.9 mV, which corresponds to a 0.95-μmol mol⁻¹ difference of oxygen fraction. Although the noise intensities at 200 kPaA and over seemed to be lower than those at 180 kPaA, we selected 180 kPaA as the sample pressure in the following experiments because the standard deviation at 180 kPaA was less than 1 μmol mol⁻¹ and the noise intensity over 180 kPaA was almost constant. Moreover, we selected the condition of 180 kPaA owing to the time required to stabilize the signal of the magneto-pneumatic oxygen analyzer from becoming longer as the pressure of the sample gas increased.

The fact that the noise intensity decreased as the pressure increased suggests that the noise mainly arose from the micro-flow sensor, because the noise intensity from the signal amplifiers usually does not depend on the amplification factors. To reduce the noise intensity, it is necessary to increase the pressure of the sample gases and to decrease the temperature. When stabilizing the signal, the pressure can be easily controlled compared to the temperature; hence, we did not attempt to maintain the sample gases at a constant temperature for low levels.

The term \((C - C_k - C_0)\) in Eq. (4) does not become zero because the oxygen fraction \(C\) varies in the actual observations. We consider the allowable variation range of the sample pressure, \(P\), for the assumed maximum value of \((C - C_k - C_0)\) to maintain the drift of signal intensity lower than 1 μmol mol⁻¹.

The pressure dependence of the signal intensity is expressed as the differential of Eq. (3) by \(P\):

\[
\frac{dS}{dP} = a \frac{(C - C_k - C_0)}{T^2}.
\]  (6)

Substituting Eqs. (5) into (6) gives

\[
dS = -\frac{T}{dP} S'(C - C_k - C_0)dP.
\]  (7)

To ensure that the drift caused by pressure variation is lower than 1 μmol mol⁻¹, \(dS\) should be less than 2 mV. The value of \(S'(C - C_k - C_0)\) is approximately -0.178V K⁻¹ cmol mol⁻¹ using the gravimetric method. The maximum difference of the oxygen fraction \((C - C_k - C_0)\) is assumed to be 1000 μmol mol⁻¹. When the temperature, pressure, and oxygen fraction differences \(|C - C_k - C_0|\) are 323 K, 180 kPaA, and 1000 μmol mol⁻¹, respectively, the relative pressure variance should be less than 0.065% for \(dS\) to be under 2 mV. The stated accuracy of the APCs is 0.5% of the full scale, and it is much larger than the required stability of 0.065%. During the measurements of Fig. 4, the pressure of the APCs fluctuated by only 2 Pa; such a fluctuation is sufficiently stable to determine the oxygen amount fraction within a 1-μmol mol⁻¹ uncertainty, and the APCs are available for atmospheric measurements of the oxygen fraction variations.

**Repeatable and long-term stability of the magneto-pneumatic oxygen analyzer**

As mentioned in the Introduction section, the oxygen analytical system comprising the magneto-pneumatic oxygen analyzer and three APCs would be suitable for continuous field-based measurements of oxygen fraction variations in the atmosphere. The repeatability of the quantification of amount fractions of oxygen and long-term stability are the most important properties for the continuous field measurements. We examined the repeatability after 90 experiments and the long-term stability of the magneto-pneumatic oxygen analyzer during five days to evaluate the applicability of the system.

The optimal conditions for the oxygen analytical system were 180 kPaA for the sample pressure and 0.192 cmol mol⁻¹ for the oxygen fraction difference between the sample and reference gases. Three gravimetrically prepared oxygen standard gases, Std6–#8 listed in Table 2, were measured with the oxygen analytical system at 4-s intervals for 4 min, and the analyzer was calibrated using the average value for these measurements. The pressures of APC1, APC2, and APC3 were 180.00, 179.97, and 300.00 kPaA, respectively. The amount fraction of oxygen in the reference gas was 19.6273 cmol mol⁻¹ to achieve a difference \((C - C_k)\) of approximately 0.192 cmol mol⁻¹. A nitrogen-balanced oxygen gas was measured and quantified with the oxygen analytical system at 4-s intervals for 4 min. This quantification procedure was repeated 90 times to evaluate the repeatability of the analytical system. The results are shown in Fig. 6. All of the data were within the range of (198050.5 ± 1) μmol mol⁻¹, and the standard deviation of was 0.42 μmol mol⁻¹. This indicates that the analytical system is quantitative enough to observe the oxygen levels in the atmosphere.

The purified air in the 47-L cylinder was measured over a period of 5 days for a long-term stability test of the oxygen analytical system. The pressure of APC1, APC2, and APC3 were set to 180.02, 180.00, and 300.00 kPaA, respectively, and the flow rate of the sample gas was approximately 100 mL min⁻¹. An oxygen standard gas mixture (oxygen fraction: 20.65 cmol mol⁻¹) prepared by the gravimetric method was used as the reference gas. Figure 7(a) shows the results of the
stability test. The output from the magneto-pneumatic oxygen analyzer was recorded every 4 s. The standard deviations of a discrete measurement and the average for a 10-min measurement were 2.7 and 1.8 mV, respectively, which correspond to 1.3 and 0.9 μmol mol⁻¹, respectively.

The temperature of the sample chamber and the experimental room during the long-term stability test are plotted in Figs. 7(c) and 7(d), respectively. The temperature of the room varies by 1.3°C during the test, whereas that of the chamber fluctuates by 0.6°C. The heat insulator wrapping the chamber reduced the variation of the temperature. However, the signal intensity fluctuated with changes in the temperature of the sample chamber. The data in Fig. 7(a) were corrected for the temperature of the chamber according to Eqs. (2) - (4). The temperature coefficient used for the correction was −0.019 V K⁻¹, which was calculated by substituting the value of $S_T'$, $C_0$, and oxygen fractions of the sample and reference gases into Eqs. (3) and (4). The results of the correction are shown in Fig. 7(b).

The standard deviations for the discrete measurement and the average for the 10-min measurement after the temperature correction were 2.4 and 1.4 mV, respectively, which correspond to 1.2 and 0.7 μmol mol⁻¹, respectively. These values are lower than the uncorrected ones. Therefore, the temperature correction based on the Eqs. (2) - (4) effectively reduced the drift of the oxygen analytical system. Although the temperature of the room varies by more than 1°C, the standard deviation of the long-term stability with the temperature correction is 0.7 μmol mol⁻¹ of amount fraction of oxygen. We thus assume that the calibration interval of the oxygen analytical system could be useful for a few days and the system can be used for continuous-field-based measurements.

Even after the temperature correction, the signal intensity drift owing to temperature variation still exists, as shown in Fig. 7(b). There seems to be a time lag between the changes in the signal intensity and the chamber temperature. The temperature measured in Fig. 7(c) is that of the sample chamber’s surface. The temperature correction should be made based on the temperature of the sample gas in the sample chamber. The reason for the time lag is probably because the temperature variations in the sample chamber’s surface are slightly delayed with respect to the change of the room temperature, whereas the temperature of the sample and reference gases follows the room temperature without any delay. The correction considering this time delay may reduce the signal intensity drift because the standard deviation for a 10-min measurement was minimized when the delay was set to 43 min. We believe that maintaining a constant temperature in the sample chamber is also essential for stabilization of the signal to achieve the uncertainty required in the GAW project.

The repeatability and stability of the oxygen analytical system were adequate for the oxygen determinations. To verify the applicability of the system, it is also necessary to consider how the water vapor and vibration, among other parameters, affect the analytical system. Samples with a low moisture concentration were used in this study. Since the magnetic susceptibility of water vapor and nitrogen is slightly different, the vapor may be an interfering component of highly accurate oxygen measurements, and this should be considered for the in-field observations.

Conclusions

An oxygen analytical system aimed for atmospheric oxygen measurements was developed. Despite the absence of pressure references and differential pressure controllers, the variance of the signal was sufficiently small to measure the oxygen variation when the oxygen fraction in the reference gases was appropriately adjusted. The repeatability of the quantification of the oxygen analytical system was 0.4 μmol mol⁻¹, and the standard deviation
for the long-term stability of the system over 5 days was 0.7 μmol mol⁻¹. Therefore, we consider that this system would be useful for field-based atmospheric measurements.

Acknowledgements

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References