

A marked improvement in the reliability of the measurement of trace moisture in gases

— Establishment of metrological traceability and a performance evaluation of trace moisture analyzers —

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The reliability of the measurement of trace moisture in a gas was improved markedly owing to the establishment of a trace moisture standard at AIST. As a result, problems with conventional methods of measuring trace moisture in gases have been revealed. This article presents the scenario that we adopted to improve the reliability of the measurement of trace moisture, development of a national trace moisture standard, provision of metrological traceability to a national standard for industrial measurements, and problems of the commercially available trace moisture analyzers as revealed through comparisons with the national standard. This improvement makes it possible to properly evaluate the quality of high-purity gases used in industry.

Keywords : Trace moisture, primary measurement standard, humidity, metrological traceability, reliability

1 Introduction

Water is an important substance without which mankind cannot survive. However, it also causes problems such as residual impurity in scientific experiments and in manufacturing processes where a high-vacuum condition or a high-purity gas is required. This is because water is present in the atmosphere in large quantities and therefore can intrude readily everywhere, and can adsorb quickly onto the surfaces of many materials. Because of these characteristics, water is considered to be an extremely troublesome impurity that is difficult to remove. Therefore, in any scientific experiment or manufacturing process, if a high-vacuum condition or a high-purity gas is required, it is necessary to address the effect of residual moisture at some point. In fact, in the field of semiconductor manufacturing, the high purity of the gas used in manufacturing is essential with the rapid progress in the integration and refinement of devices, and the control of trace-level residual moisture in the gas has become a major issue. For example, in the case of the high-purity nitrogen gas used to prevent contamination of the wafer surface, the control of residual moisture to several nmol/mol (ppb) or less in amount-of-substance fraction (mole fraction) is considered necessary^[1], corresponding to a frost point^{Term 1} of -100 °C or less at atmospheric pressure. As another example, in the case of a gallium nitride (GaN) light-emitting diode, a significant decrease in light-emitting efficiency was observed in the presence of trace residual moisture of 1 μmol/mol (ppm) or less^[2] in an NH₃ gas used in the film growth by metal-organic vapor-phase epitaxy (MOVPE). In any case, a highly reliable moisture measurement is essential to control the trace level of moisture and to correctly assess the effect of residual moisture.

Figure 1 shows the humidity range for which the national standard has been established in Japan. Several types of measuring instruments^[3] for measuring the moisture content in gas (humidity) at various ranges are available commercially and are used in many production sites and scientific experiments. However, in the range of trace moisture of 1 μmol/mol (ppm) or less, the measured value of humidity may vary with the instrument used even if the measurement is performed under the same conditions. When such issues arise, they are usually resolved by calibrating the measuring instruments on the basis of the national standard, but there has been no national standard in the trace moisture region until recently, and the calibration of instruments is not straightforward. Hence, when the calibration is essential, the users or measuring instrument companies have had to attempt the calibration by some method that they devised on their own. However, the mismatch of values indicated by the instrument occurred frequently even when the calibration was performed in this way, and the measurements of trace moisture have not been particularly reliable.

To settle this issue, the National Institute of Advanced Industrial Science and Technology (AIST) established the national standard for trace moisture (trace moisture standard); the standard with the highest metrological quality called the primary measurement standard,^{Term 2} which is directly traceable to the International System of Units (SI), was developed. Furthermore, a system for providing the trace moisture standard (calibration service) was organized, as illustrated in Fig. 2. In the process of developing the trace moisture standard, it was found that a new trace moisture analyzer based on cavity ring-down spectroscopy (CRDS) had

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excellent capability for measuring trace moisture. Because of these three reasons, namely, the national standard for trace moisture was established, the calibration service system traceable to the SI was organized, and a high-performance measuring instrument became available commercially, the reliability of trace moisture measurement has very recently increased markedly. Simultaneously, the problems concerning the methods conventionally used for measuring trace moisture have been revealed.

This paper describes the scenario adopted by AIST for increasing the reliability of trace moisture measurement, research activities toward achieving this objective, and the recent changes in the reliability of trace moisture measurement brought about by the results of this research.

2 Scenario and objective of increasing the reliability of trace moisture measurement

To maintain the high reliability of trace moisture measurement in the production sites and scientific experiments, the following are necessary: (1) establishment of a national standard for trace moisture as the basis of the scale of the trace moisture analyzer, (2) organization of a calibration service for measuring instruments, and (3) a high-performance measuring instrument that can be used for the trace moisture measurement in the production sites or scientific experiments. The relationships among these three factors are shown in Fig. 3. The issues that must be resolved to realize (1)-(3) are shown in the second column from the left, and are connected by arrows to (1)-(3). These issues must

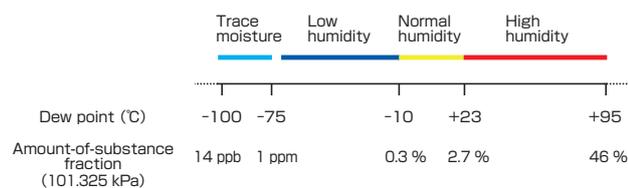


Fig. 1 Current state of calibration service for moisture in gas (humidity) in Japan.

The calibration service for the frost point range between -75 °C and -70 °C is currently in preparation.

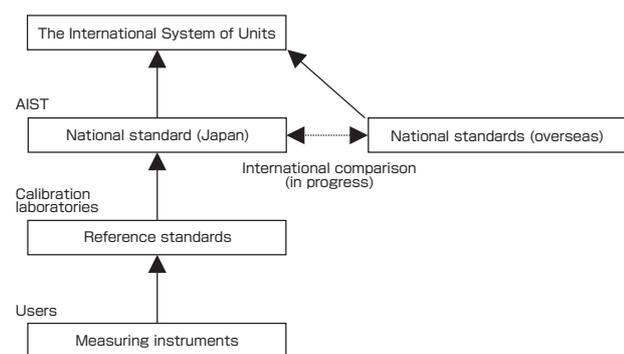


Fig. 2 Traceability system for trace moisture measurement.

be solved by national metrology institutes, calibration service providers, and measuring instrument manufacturers. In the figure, the arrows connect the issues that each party must tackle. In the relationships among (1)-(3), it is important to organize the calibration service system traceable to the SI, and it is extremely effective to demonstrate the measurement capability of the instrument on the basis of an experiment in which the traceability to the national standard is maintained. Therefore, we considered (1) as the priority among the three. Because (1) was an issue that must be addressed by national metrology institutes, AIST initiated research to establish the trace moisture standard in a gas (nitrogen) in 2001. The goal for the lower limit of trace moisture was set as 14 nmol/mol (ppb), corresponding to a frost point of -100 °C at atmospheric pressure, and the upper limit was set as 1 μmol/mol (ppm), corresponding to -75 °C, considering the lower limit of the frost point achievable using the current frost point generator at AIST. The measurement uncertainty was set as a relative standard uncertainty of 11 %, corresponding to 0.5 °C around the frost point of -100 °C. This figure surpasses the standard uncertainty of 0.5 °C at a frost point of -95 °C that was set as a goal by the National Physical Laboratory (NPL) of UK at that time^[4]. For (2), we planned, for some time immediately after the establishment of the standard, that the calibration service would be provided directly by AIST to individual users upon request using the national standard, and that calibration service providers would be recruited at the same time. For (3), we planned, after the establishment of the national standard, that the evaluation of the measuring instrument would be performed using the national standard to find instruments demonstrating high performance. Research activities performed in line with this scenario are described below.

3 Establishment of the national standard for trace moisture

The national standard for trace moisture can be realized with a generator that generates gas containing a certain amount of moisture with a known standard value (trace moisture generator), and then performing the uncertainty evaluation of the standard value. When establishing a national standard,

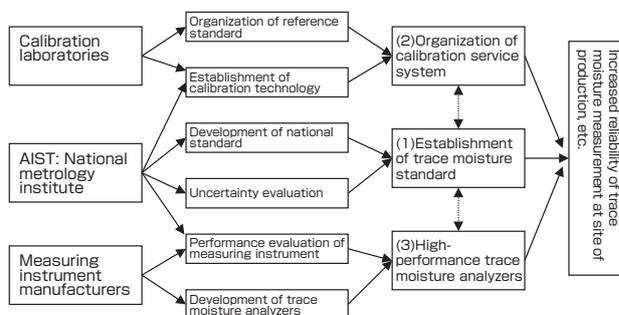


Fig. 3 Scenario for elemental technologies and integration to increase the reliability of trace moisture measurement.

the traceability to the SI may be guaranteed by calibrating the standard using a national standard of the same quantity established in another country, and many developing countries often select this method. In contrast, many advanced countries develop a standard called a primary measurement standard that is directly traceable to the SI. The method adopted depends on the technology, cost, and level of the domestic industry. Because there are advanced semiconductor and process industries in Japan, AIST decided to develop its own primary measurement standard.

Another very important task is selecting the generation method for the trace moisture generator. Here, AIST selected a unique method, different from those of national metrology institutes of other countries. The reasons were because we had a specific plan for this unique method, we considered it possible to achieve the world's highest precision if this unique method was successful, and the reliability of the standard could be increased by maintaining multiple national standards using different methods around the world, rather than relying on a single method.

3.1 Selection of the generation method

There are several methods of generating trace moisture, and AIST selected a method called the diffusion tube method. Figure 4 shows a schematic diagram of the trace moisture generator using the diffusion tube method^[5]. A diffusion cell is composed of a small water vessel and a diffusion tube made of metal such as stainless steel, and this is placed in the generation chamber under controlled temperature and pressure. The water vessel of the cell contains water, and water vapor with pressure that responds to a given temperature is generated inside the vessel. The vapor passes through the diffusion tube and travels to the generation chamber. Trace moisture is generated by mixing the vapor with flow-controlled dry gas in the chamber. The amount-of-substance fraction of water in the gas is determined by measurement of the mass of moisture that evaporates per unit time (evaporation rate) and the mass of dry gas that flows per unit time (flow rate).

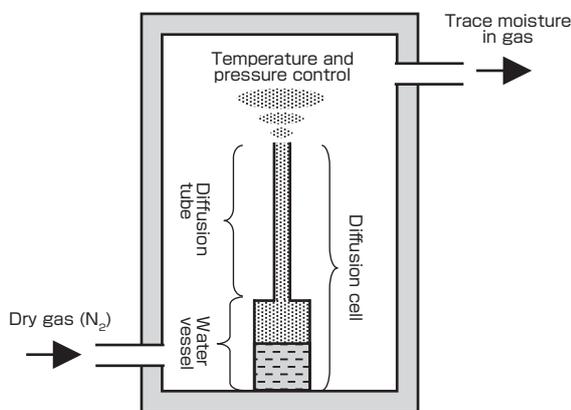


Fig. 4 Schematic diagram of diffusion-tube trace-moisture generator.

Table 1 Comparison of diffusion tube method and frost point generation method.

Generation method	Diffusion tube	Frost point
Achievement and check of saturation	Not necessary	Necessary
Vapor pressure equation and enhancement factor	Not necessary	Necessary
Measurement of extremely small mass loss rate	Necessary	Not necessary
Zero gas	Necessary	Not necessary
Past performance as a primary standard	No	Yes

National metrology institutes other than AIST commonly employ a method called the frost point method as the core of their low-humidity and trace moisture generation system. Figure 5 shows a schematic diagram of the frost point generator. A gas is passed through a saturation chamber that is saturated with water vapor evaporated from ice at a constant temperature, and humid gas is generated by mixing the vapor and gas. When saturation is complete and the state of equilibrium is achieved, humid gas with a frost point equivalent to the temperature of ice is generated. Trace moisture can be generated using low-temperature ice (-75 °C or less). The amount-of-substance fraction of water in the generated gas is determined by measuring the ice temperature, the pressure inside the generation chamber, as well as the vapor pressure formula of ice and the enhancement factor of ice^{Term 3 [6][7]}. Although the principle of this method is simple, it is highly reliable for generating humidity.

Table 1 gives a comparison of the advantages and disadvantages of the two methods. One of the advantages of the diffusion tube method is that it does not require the achievement and confirmation of saturation, which are necessary in the frost point method. In the frost point method, complete saturation in the saturation chamber is necessary, but the state of equilibrium is difficult to achieve in the low-temperature range because the amount of vapor

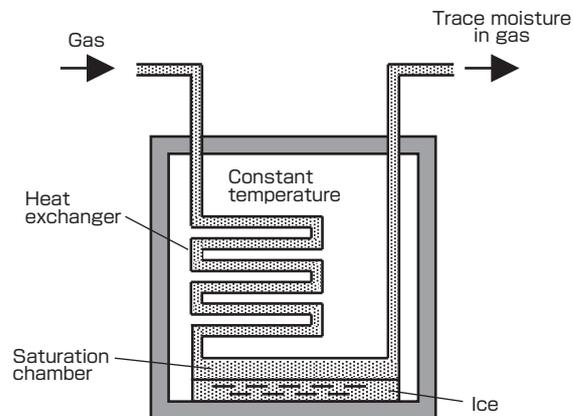


Fig. 5 Schematic diagram of frost point generator.

from ice decreases with the decrease in temperature, and it becomes more sensitive to external thermal stimuli as the vapor pressure becomes more susceptible to temperature change. Moreover, even when saturation is achieved, it is not easy to confirm the state of equilibrium, and therefore, a large degree of uncertainty must be taken into account. These issues can be avoided in the diffusion tube method. For determining the amount-of-substance fraction of water in the generated gas, the frost point method requires the vapor pressure formula and enhancement factor. In contrast, the diffusion tube method does not suffer from this problem, because this method can be used to determine the amount-of-substance fraction of water in the gas from the measurements of the evaporation rate and flow rate, and therefore, it is a method clearly traceable to the SI to generate a humid gas with a known amount-of-substance fraction of water. Because Sonntag's equation,^{[7][8]} which is often used as the vapor pressure formula for ice, is only effective down to -100 °C, the amount-of-substance fraction of water cannot be determined when Sonntag's equation is used for temperatures below -100 °C in the frost point method. Moreover, there have been no reports of experiments using the enhancement factor below -35 °C, and it has been pointed out that the extrapolation of the formula is unreliable below this temperature^[9]. This is not an issue for the diffusion tube method, which neither requires the vapor pressure formula nor the enhancement factor.

However, there are disadvantages in the diffusion tube method, one of which is the need to measure a very small evaporation rate. For the generation of trace moisture of 14 nmol/mol (ppb) using the diffusion tube method, the evaporation rate becomes extremely small, approximately 14 µg/h (≈780 nmol/h) when the dry gas is nitrogen and the flow rate is 20 L/min (at 0 °C and 101.325 kPa); the key is how this evaporation rate can be measured with as small uncertainty as possible. There is also the problem of zero gas. In the diffusion tube method, the moisture remaining in the dry gas may generate uncertainty, and it is necessary to prepare a dry gas called zero gas where the moisture content is lowered to as close to zero as possible. Another problem is that there have been no previous reports in which the diffusion tube method was established as a primary measurement standard of trace moisture. This meant that little of the knowledge, experience, or technology needed for the standard establishment has been accumulated, and it was necessary to design the instrument and develop the analysis method of the uncertainty almost from scratch.

After carefully reviewing the advantages and disadvantages of the diffusion tube and frost point methods, AIST selected the diffusion tube method, as already mentioned. There were four primary reasons for selecting this method, as follows. First, the realization and confirmation of saturation required in the frost point method were considered problematic.

Investigation of the development of the trace moisture standard started in around 1999 at AIST (formerly, National Research Laboratory of Metrology, Agency of Industrial Science and Technology), but some national metrology institutes in other countries had already started developing the trace moisture standard on the basis of the frost point method. However, to the best of our knowledge, there was no published research at that time that reported the uncertainty of the trace moisture standard around the frost point of -100 °C on the basis of measurement traceable to the SI and that described the analysis method of uncertainty evaluation. We considered that this was attributable to the difficulty in the realization and confirmation of perfect saturation around -100 °C. Second, the direction of future trace moisture measurement was considered. According to the International Technology Roadmap for Semiconductors 2000^[10], the level at which trace moisture must be controlled had already been reported to be equivalent to the frost point of -100 °C or less, and it stated that controlling residual moisture in the lower frost point range will be required in the future. We considered that the reliability of the vapor pressure formula and enhancement factor would become issues when the frost point method is used in this range. The third reason was the development of a new balance called the magnetic suspension balance^[11]. This balance became commercially available in the early 1990s, and many research studies using this balance were published from the middle to late 1990s. By 2000, it was demonstrated that this balance has excellent performance and usability, and we considered that the difficulty in measuring the very small evaporation rate in the diffusion tube method could be overcome through the use of the magnetic suspension balance. Finally, as metrologists, we find the clear traceability to the SI of the diffusion tube method very fascinating.

3.2 Development of the primary measurement standard

The amount-of-substance fraction of the trace moisture in the gas generated by the trace moisture generator using the diffusion tube method is given as

$$x_w = \frac{N + N_b + Fx_b}{N + N_b + F} \approx \frac{N}{F} + \frac{N_b}{F} + x_b \quad (1)$$

where

x_w : Amount-of-substance fraction of trace moisture in generated gas [mol/mol]

N : Amount-of-substance of moisture generated as vapor from diffusion tube per unit time [mol/h]

N_b : Amount-of-substance of moisture that moves by adsorption/desorption per unit time [mol/h]

F : Flow rate of dry gas per unit time [mol/h]

x_b : Amount-of-substance fraction of residual moisture in dry gas (zero gas) [mol/mol]

The strategy of developing the primary measurement standard by the diffusion tube method can be described using Eq. (1) as follows. The measurement method for each of the physical quantities on the right side of Eq. (1) is established. A generator is developed to fulfill the conditions $x_w \gg x_b$ and $N \gg N_b$ at $x_w \sim 14$ nmol/mol and $N \sim 780$ nmol/h, and Eq. (1) can be approximated as

$$x_w \approx \frac{N}{F} \quad (2)$$

N and F are stabilized (their variabilities are reduced). A technology is developed to measure N and F with small uncertainty, and the standard value x_w can be determined using Eq. (2).

However, the actual development was not performed in this order. There were several technologies, both major and minor, that had to be developed, and when advances in one technology were achieved, other technologies had to be revised. The development did not progress in one direction only.

3.2.1 Measurement of evaporation rate

N in Eq. (2) can be obtained by measuring the evaporation rate [g/h] and by dividing it by the molar mass of water (18.02 g/mol). As mentioned in section 3.1, we planned to use a magnetic suspension balance for the measurement of the evaporation rate. The magnetic suspension balance is structured so that the diffusion cell placed inside the generation chamber is suspended on an exterior electronic balance by a magnetic force. By using this balance, the mass-loss rate of the diffusion cell owing to water evaporation (evaporation rate) can be measured continuously without interrupting the generation of water vapor. The magnetic suspension balance at AIST was specially customized for the development of the trace moisture standard; the inner surface of the balance in contact with the gas is electropolished because it is part of the generation chamber; the balance can measure a change in mass of the diffusion cell of

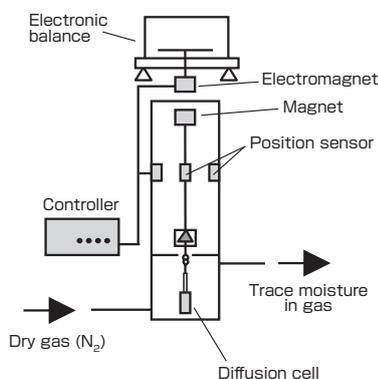


Fig. 6 Schematic diagram of mass loss measurement of diffusion cell using magnetic suspension balance.

approximately 12 g at 1 μ g resolution; the indication of the balance can be calibrated using external weights traceable to the SI, and so forth. Figure 7(a) shows an example of a measurement using the magnetic suspension balance. It can be seen that a small evaporation rate of 5.1 μ g/h can be measured with sufficient accuracy. Figure 7(b) shows an example of a measurement without using the magnetic suspension balance. The generation chamber was exposed to the atmosphere at each mass measurement of the diffusion cell, and the diffusion cell inside the generation chamber was measured by suspending it using a wire connected to the hook of the electronic balance placed above the generation chamber. The diffusion cell used was the same as that shown in Fig. 7(a). For further details of the experiment, refer to Ref. [12]. In this case, an evaporation rate of 6.6 μ g/h was measured, and it appeared that this method would suffice except for the fact that it was time-consuming. In fact, the diffusion tube method is often used as a simple trace moisture standard, after the evaporation rate has been determined in advance using gravimetry without using a magnetic suspension balance in a manner similar to that described above. This evaporation rate was used as a constant value under the same experimental conditions, in particular, temperature and pressure. However, from the comparison with values calculated theoretically, a problem was found in the experiment illustrated in Fig. 7(b). Assuming ideal diffusion in the diffusion tube method, the evaporation rate can be calculated from the inner diameter and length of the diffusion tube, the pressure in the generation chamber, and the temperature of the water inside the cell. The details of the calculation method are provided in Ref. [5]. In the case of the experiment illustrated in Fig. 7(b), the theoretical value was 4.1 μ g/h, which differed slightly from the measured value. This difference could not be explained on the basis of the uncertainty of pressure, temperature, or other factors. In the experiment using the magnetic suspension balance (Fig. 7(a)), the theoretical value was 5.1 μ g/h, which was consistent with the measured value. To confirm that this was not a coincidence, we performed experiments using diffusion tubes with different inner diameters and different pressures and temperatures in the generation chamber, and it was found that the theoretical and measured values were consistent

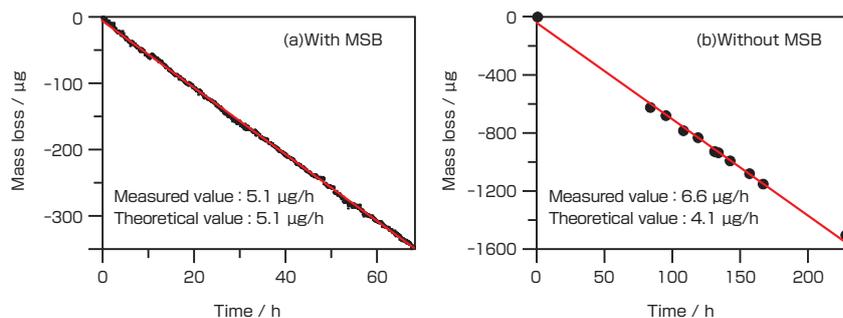


Fig. 7 Data of mass loss measurement of diffusion cell. MSB stands for magnetic suspension balance.

with each other within the uncertainty^[5]. From this result, it was demonstrated that the magnetic suspension balance was extremely effective for reliably measuring an evaporation rate at the 10 $\mu\text{g}/\text{h}$ level. Another finding from this result was that the evaporation in the generator could be explained on the basis of the diffusion phenomenon. This indicates that N in Eq. (2) can be sufficiently stabilized by controlling the temperature and pressure. This was also confirmed experimentally, and a stability within a relative standard uncertainty of 0.6 % was realized by precise temperature and pressure control^[5]. It is interesting to note that the technology developed for the measurement of N led to the technology required for the stabilization of N .

3.2.2 Measurements of adsorbed and desorbed moisture and residual moisture in zero gas

Measurements of N_b and x_b were necessary to develop a trace moisture generator that fulfills the conditions $x_w \gg x_b$ and $N \gg N_b$ of Eq. (1) even for $x_w \sim 14$ nmol/mol (ppb) and $N \sim 780$ nmol/h, and a high-performance trace moisture analyzer was necessary for this purpose. To address this issue, we initially considered using the vacuum ultraviolet fluorescent trace moisture analyzer (VUV)^[13] developed at the National Research Laboratory of Metrology and the atmospheric pressure ionization mass spectrometer (APIMS)^[3] that was introduced in 2000. VUV is an instrument that detects the fluorescence emitted from OH radicals in an electronic excited state produced by the photolysis of water molecules using vacuum ultraviolet absorption. APIMS is an instrument that detects a trace substance (in this case, trace moisture) in a gas by ionizing the sample gas using a corona discharge under atmospheric pressure, and then introducing the gas into a mass spectrometer by differential evacuation. Both VUV and APIMS are sufficiently sensitive in the trace moisture region, but the instrument itself is not scaled, and it is necessary to create a calibration curve using a standard. We considered creating the calibration curve by a standard addition method using trace moisture generated

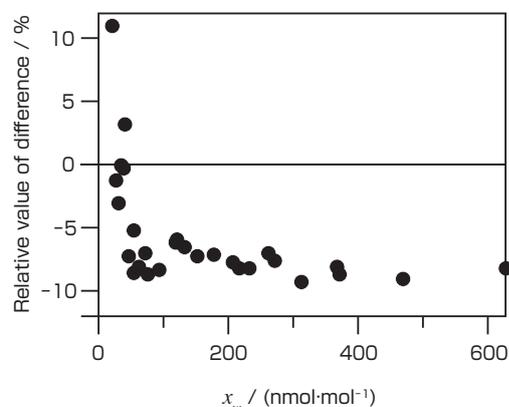


Fig. 8 Difference between indication of CRDS trace moisture analyzer and standard value (relative value). The dots represent $[(\text{indication} - \text{standard value}) \div \text{standard value}] \times 100$.

by the diffusion tube generator that was being developed. That is, assuming that N_b and x_b of Eq. (1) maintain constant values, x_w is varied by changing N and F , the indications of VUV or APIMS are recorded, and the calibration curve is created from the relationship of the differences between the N and F values and the indications. However, in the trace moisture range, because a long time was necessary for dry purging (the removal of residual moisture) after exchanging the diffusion cell (to change N), the baseline drift and sensitivity drift of VUV or APIMS during the experiment period could not be ignored because of their non-negligible magnitudes compared with the signal intensity. Moreover, it was unknown how much dry-purging time was necessary to ensure that N_b was the same as that before the exchange, and it was also unclear whether N_b could be considered to be approximately constant after dry purging. Therefore, as the research progressed, we found that it was difficult to create a reliable calibration curve using this method in the trace moisture region.

In the trace moisture region, because we expected that the uncertainty due to adsorption/desorption moisture and residual moisture in zero gas would strongly dominate in the total uncertainty, we considered the measurement of N_b and x_b to be particularly important in developing the generator. As the research progressed, we began to consider that it was problematic to use only VUV and APIMS.

Around that time (about 2002), a new trace moisture analyzer based on the cavity ring-down laser spectroscopy (CRDS)^{[14]-[17]} became commercially available. CRDS is a method where a laser pulse is coupled into an optical cavity composed of two high-reflectivity mirrors, and the detection sensitivity is increased through a long optical path length generated by bouncing the laser pulse back and forth between the mirrors. The sensitivity of this method of absorption spectroscopy has increased markedly in recent years. Because x_w can be calculated directly from the absorption cross section

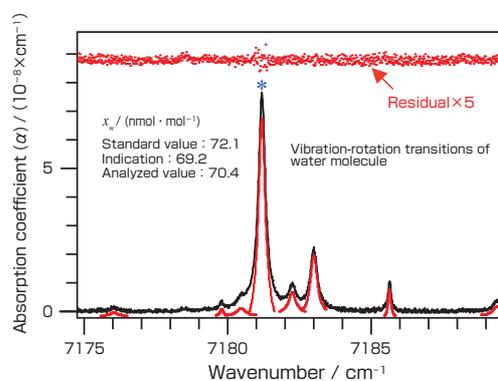


Fig. 9 Near-infrared spectrum of water.

All absorption lines in the figure are assigned to the vibration-rotation transitions of water molecule. The amount-of-substance fraction of water is determined using the $2_{02} \leftarrow 3_{03}$ transition of the $\nu_1 + \nu_3$ band that is the strongest in the figure (marked with asterisk).

of the water molecule and measurement data obtained using the CRDS trace moisture analyzer, trace moisture can be measured without a calibration curve. Because this characteristic was considered an advantage over VUV or APIMS, we immediately started to gather information on the instrument performance and introduced it in early 2003. According to the calibration certificate issued by the instrument manufacturer, the accuracy of the indications of the CRDS trace moisture analyzer was confirmed in the range of 0 nmol/mol (ppb) to 1000 nmol/mol (ppb) using a reference standard traceable to NIST of the United States. To check the accuracy of the indications independently, a trace moisture gas with a known value (standard value) generated by the AIST trace moisture generator was measured using the CRDS trace moisture analyzer (indication), and the indications and standard values were compared^[5]. Figure 8 shows the differences between the indications and standard values as relative values. In addition, absorption spectra were measured using a built-in function of the CRDS trace moisture analyzer, and x_w was calculated from the analysis of the absorption line (analyzed value). Figure 9 shows a measured spectrum. The absorption lines in Fig. 9 are assigned to the vibration-rotation transitions of the water molecule, and the strongest absorption line shown in the figure ($2_{02} \leftarrow 3_{03}$ transition of $\nu_1 + \nu_3$ band) was used for the analysis. The indications of the CRDS trace moisture analyzer were determined on the basis of the peak intensity of this absorption line. The three x_w values obtained independently agreed within 11 % in the range of 20 nmol/mol (ppb) to 600 nmol/mol (ppb), and it was found that the CRDS trace moisture analyzer can be used for the measurement of N_b and x_b . Using the CRDS trace moisture analyzer, we found methods of achieving $x_b < 0.15$ nmol/mol (ppb) and $N_b < 6$ nmol/h and of establishing a technology to fulfill the conditions $x_w \gg x_b$ and $N \gg N_b$. In the process of this research, it was also demonstrated that the CRDS trace moisture analyzer was a high-performance measuring instrument.

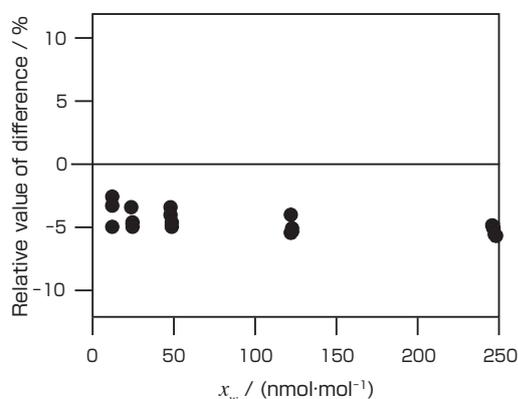


Fig. 10 Difference between indication of CRDS trace moisture analyzer and standard value after introduction of critical flow Venturi nozzle flow meter (relative value). The dots represent $[(\text{indication} - \text{standard value}) \div \text{standard value}] \times 100$.

3.2.3 Measurement of dry gas flow rate

The flow rate F of the dry gas (nitrogen) is controlled and measured using a thermal mass flow meter. We initially considered calibrating the flow meter to obtain the traceability to the SI using the Japan Calibration Service System (JCSS)^[18], introduced in Japan by the Measurement Act. In late 2004, we asked the technical staff of the calibration laboratory accredited by JCSS who was capable of calibrating flow meters with the smallest uncertainty, but they replied that they had not yet had any experience of calibrating the thermal flow meter, and that they were not yet confident in performing the calibration. At that time, the accuracies of thermal flow meters stated by the manufacturers were generally 1 % of the full scale, and the uncertainty increased markedly in the small flow range relative to the full scale of the flow meter. This meant that it was necessary to set up several flow meters and calibrate all of them in order to cover the entire flow range with the small uncertainty needed in this research. Moreover, we considered that the differences in the indications and standard values observed in Fig. 8 originated mainly from the uncertainty of the flow rate measurement. For the above reasons, from about the first half of 2005, we started to consider using a flow meter with a high reliability based on a different principle.

For the measurement of a small gas flow, the most reliable flow meter is considered to be a critical-flow Venturi nozzle (sonic nozzle) mass flow meter^{[19][20]}. The critical-flow Venturi nozzle flow meter was developed through joint research between the National Research Laboratory of Metrology and a flow meter manufacturer^[21] and it became commercially available in around 2000. We introduced this type of flow meter in 2005, and the traceability to the SI was established using the JCSS. The flow rate was calculated independently using the measurements of the pressure and temperature of the gas and the information on the size of nozzle, and the operating principle was checked through the comparison between the calculated values and the indications of the flow meters. From experiments using these flow meters and by adding some improvements in controlling the flow rate, it

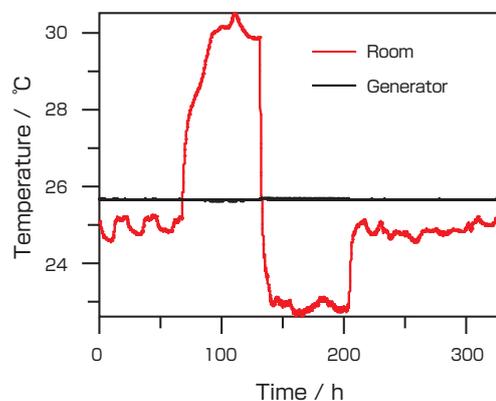


Fig. 11 Change of generation chamber temperature against change of room temperature.

was confirmed that flow rate control at a standard uncertainty of within 0.15 % was achievable^[22]. Figure 10 shows the result of the comparison between the standard values of the trace moisture after introducing the critical-flow Venturi nozzle flow meters and the indications of the CRDS trace moisture analyzer. As in Fig. 8, the differences between the indications and standard values are shown as a relative value. The figure shows that the differences are within 6 % and are almost constant, in contrast to the result shown in Fig. 8 where the maximum difference reached 11 %. The remaining difference in Fig. 10 can be explained on the basis of the uncertainty due to the effect of the temperature on the absorption cross section and that due to the inaccurate value of the absorption cross section used in the CRDS trace moisture analyzer^[22].

3.3 Evaluation of uncertainty

The standard uncertainty $u(x_w)$ of x_w can be expressed as follows, assuming that there is no correlation between the physical quantities on the right side of Eq. (1):

$$u(x_w) = \sqrt{\left(\frac{u(N)}{F}\right)^2 + \left(\frac{u(N_b)}{F}\right)^2 + \left(\frac{Nu(F)}{F^2}\right)^2 + u^2(x_b)} \quad (3)$$

$u(A)$ on the right side represents the standard uncertainty of physical quantity A . Moreover, $u(A)$ can be expressed as

$$u^2(A) = c_1^2 u^2(a_1) + c_2^2 u^2(a_2) + \dots \quad (4)$$

where c_i is the sensitivity coefficient and $u(a_i)$ represents the standard uncertainty of physical quantity a_i . c_i can be determined by theoretical consideration or by experiment. It is also important to identify what physical quantities should be included in Eq. (4) as $u(a_i)$. Minor uncertainties can be ignored. However, it often takes considerable time to determine which uncertainties can actually be ignored. There are also cases where an uncertainty component considered to be negligible was in fact not negligible. In one example, we observed variability in the evaporation

rate when measurements were performed several times, but this variation could not be explained on the basis of the variabilities of the pressure and temperature in the generation chamber. After gathering long-term data, we found a correlation between the evaporation rate and the room temperature, and we performed an experiment where the temperature of the room was varied intentionally using an air conditioner. Figure 11 shows the temperatures of the room and generation chamber recorded during the experiment. Although the temperature of the chamber appeared to remain constant even if the room temperature was varied, the evaporation rate measured using the magnetic suspension balance depended on the room temperature, as shown in Fig. 12(a). In order to verify that this was not an effect of temperature on the indication of the magnetic suspension balance that biased the measurement value but the effect of temperature on the evaporation rate, we also examined the effect of temperature on the indication of the CRDS trace moisture analyzer shown in Fig. 12(b). The indication of the CRDS trace moisture analyzer clearly depended on the room temperature (the bias of the indication due to the temperature change was compensated), and we concluded that the temperature affected the evaporation rate. The sensitivity coefficients for the change in evaporation rate against the change in room temperature obtained from data shown in Figs. 12(a) and 12(b) were consistent. This phenomenon is probably attributable to unexpected heat transfer, for instance, through the dry gas introduced into the generation chamber. Furthermore, the temperature of the point monitored using a thermometer (controlled to be a set value) may differ from the temperature of the water in the diffusion cell (affected by the variability of room temperature). Further details of this temperature effect were discussed in Ref. [23]. Because it appeared that the temperature of the generation chamber was well controlled, we considered that the temperature of the water in the diffusion cell was also well controlled, and we did not initially recognize this uncertainty component. However, from the above experiment, we found that the uncertainty component due to the variability of room temperature should be included in $u(N)$ as $u(a_i)$, and its

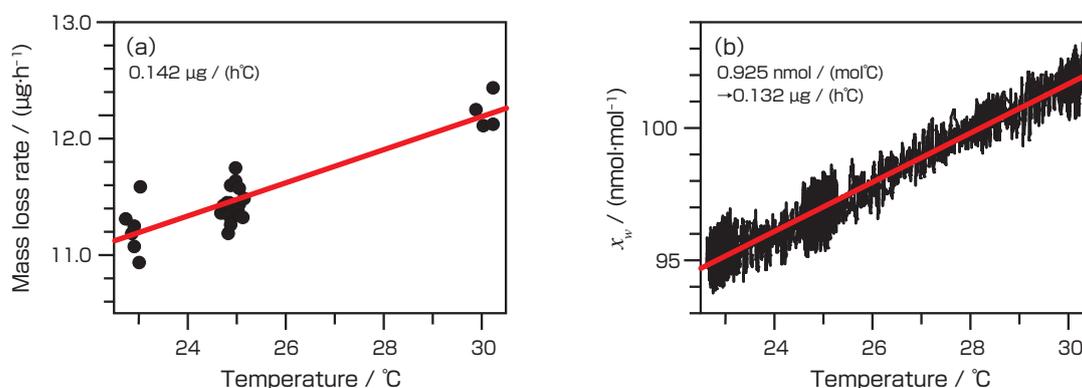


Fig. 12 Room temperature dependency of evaporation rate.
Reproduced with permission from Ref. [23].

sensitivity coefficient was determined from the experiments.

The process of evaluating uncertainty involves completing Eqs. (3) and (4) by similarly evaluating the uncertainties of other physical quantities in the two equations by an experimental or theoretical consideration. In this process, a table of uncertainty evaluation is normally created to organize and visualize the results. The uncertainty evaluation is complete only when this table is filled. The table of uncertainty evaluation that we completed in this research is shown in Table 2 (including uncertainty components in Eq. (3) only). Generally, in establishing a standard, uncertainty evaluation is as difficult as or more difficult than the development of the instruments used in the standard.

3.4 Summary of establishment of the trace moisture standard

From the results shown in sections 3.2.1-3.2.3, we finally succeeded in developing a trace moisture generator that can generate trace moisture in the range between 12 nmol/mol (ppb) and 1200 nmol/mol (ppb) (corresponding to a frost point between -100 °C and -75 °C at atmospheric pressure), and we achieved the goal for the generation range. An uncertainty of about 3 % was achieved, as seen in Table 2, surpassing the target of 11 % for the relative standard uncertainty at 12 nmol/mol (ppb). Thus, the trace moisture standard was established as intended.

In this research, we consider that the selection of measuring instruments was extremely important. Without the magnetic suspension balance, CRDS trace moisture analyzer, and critical-flow Venturi nozzle flow meter, we believe that the establishment of the trace moisture standard would have been extremely difficult. One key to success was that, although the CRDS trace moisture analyzer and critical-flow Venturi nozzle flow meter were initially not considered, we were able to notice the problems in the instruments used initially in the relatively early stage of the research and were able to introduce new instruments relatively soon after that. Another key factor was attributable to the effort spent on customizing the instruments used in this research. Although not hitherto mentioned in this paper, we adequately discussed our special requirements with the manufacturers before installing their instruments and also the improvement as needed after installation.

4 Preparation of the calibration service system

On the basis of the trace moisture standard established in this research, AIST initiated the calibration service for measuring instruments in the range between 12 nmol/mol (ppb) and 240 nmol/mol (ppb) (a frost point in the range between -100 °C and -85 °C at atmospheric pressure) in May 2007. The calibration range was expanded in May 2009, and we now provide a calibration service for the range from 12

Table 2 Evaluation table for uncertainty of trace moisture generation*.

Standard value	12.00	20.00	50.00	100.00	500.0	1200.0
Uncertainty component						
· Evaporation rate	0.172	0.286	0.715	0.384	1.918	4.602
· Adsorbed/desorbed moisture	0.014	0.024	0.059	0.021	0.104	0.249
· Flow rate of dry gas	0.024	0.040	0.099	0.198	0.990	2.376
· Residual moisture in zero gas	0.300	0.300	0.300	0.300	0.300	0.300
Combined standard uncertainty	0.35	0.42	0.78	0.53	2.2	5.2
Relative combined standard uncertainty (%)	2.9	2.1	1.6	0.53	0.44	0.43

*All units are in nmol/mol (except relative combined standard uncertainty)

nmol/mol (ppb) to 1200 nmol/mol (ppb) (a frost point in the range between -100 °C and -75 °C at atmospheric pressure). The Chemicals Evaluation and Research Institute (CERI) developed a trace moisture generator using a diffusion tube method without a magnetic suspension balance, and using the CRDS trace moisture analyzer as a reference standard for obtaining the traceability to AIST, they initiated a calibration service for the range between 12 nmol/mol (ppb) and 1200 nmol/mol (ppb) in July 2009.

5 High-performance trace moisture analyzer

Even if a trace moisture standard and calibration service are available, highly reliable measurement cannot be realized without a high-performance trace moisture measuring instrument, and the task of finding such an instrument is necessary. Here, the results of a preliminary performance test using the AIST trace moisture standard on some commercially available trace moisture analyzers are described.

5.1 Performance test on CRDS trace moisture analyzer

As mentioned in section 3.2.2, in the process of establishing the standard, we found that the CRDS trace moisture analyzer has an excellent performance in measuring trace moisture. Figure 13 shows an example of the measurement of trace moisture using the CRDS trace moisture analyzer. It is demonstrated that the CRDS trace moisture analyzer has good response and stability. The result also demonstrates the good response and stability of trace moisture generation using the AIST standard generator. It was confirmed that the CRDS trace moisture analyzer is capable of measuring trace moisture as low as about 1 nmol/mol (ppb) with excellent linearity in the range between 12 nmol/mol (ppb) and 1400 nmol/mol (ppb) from the comparison with the standard.

5.2 Performance tests on other commercial measuring instruments

A similar performance test was carried out on some conventional chilled-mirror hygrometers. The tested hygrometers were the products of two companies, and the lower limit of the measurement range specified in the catalogs was a frost point of -100 °C (14 nmol/mol (ppb)) or less for both products. The results are shown in Fig. 14. In this test, the product of Company A presented problems

in the accuracy and stability of the indications, while the product of Company B showed problems in response and accuracy. Because a chilled-mirror hygrometer can directly measure the frost point, it has the highest reliability among instruments measuring humidity. However, it was demonstrated from this result that the measurement in the trace moisture range was not straightforward, even with the chilled-mirror hygrometer.

Performance tests were carried out on some conventional aluminum oxide capacitive sensors that are widely used in industry. The products of five companies were tested, and the lower limit of the measurement range specified in the catalogs was a frost point of $-100\text{ }^{\circ}\text{C}$ (14 nmol/mol (ppb)) or less for all the products. The flow rate of gas introduced into the sensor was 0.6 L/min to 1.0 L/min, and dry purging (the removal of residual moisture) was performed for over one month before the test using the trace moisture of 12 nmol/mol (ppb). The long purging period was set to investigate the performance under actual conditions, because conventional aluminum oxide capacitive sensors are often used as an alarm indicating the presence of moisture in the processes that involve drying, and the sensors are exposed to an extremely dry atmosphere for a long time. The test was performed in the range of between approximately 12 nmol/mol (ppb) and 100 nmol/mol (ppb) (a frost point between about $-100\text{ }^{\circ}\text{C}$ and $-90\text{ }^{\circ}\text{C}$). The product of one of the five companies indicated an error, that the level of moisture was below the

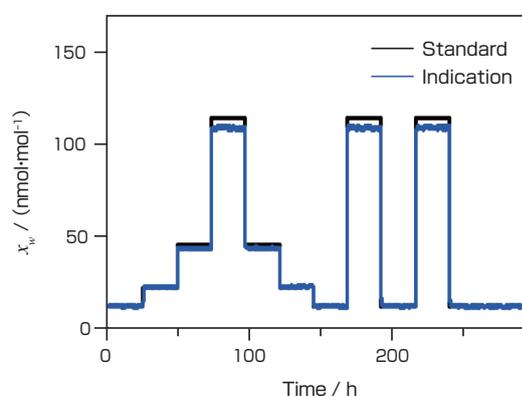


Fig. 13 Comparison of standard value and indication of CRDS trace moisture analyzer.

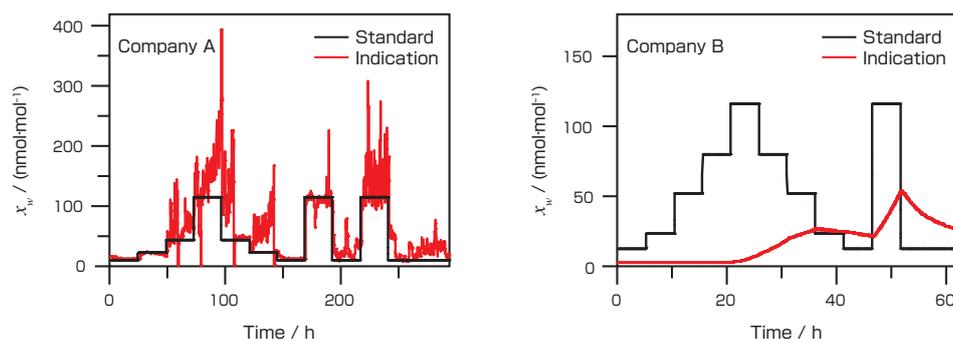


Fig. 14 Comparison of standard value and indication of chilled-mirror hygrometer.

measurement range, and measurement was not possible. The results of the products of the other four companies are shown in Fig. 15. The sensors exhibited problems in response, accuracy, and sensitivity of the indications. Similar tests were performed in joint research between BOC Edwards, Ltd. and NPL, and it was reported that some sensors required 8 h or more to respond to the moisture concentration change of 300 nmol/mol (ppb) \rightarrow 850 nmol/mol (ppb)^[24]. Because the conventional aluminum oxide capacitive sensor uses the equilibrium of moisture adsorption in the pores of aluminum oxide, it is deduced that the slow response is responsible for the long time required to reach the equilibrium state in the trace moisture range. Therefore, technological development to increase the response is necessary for the measurement using conventional aluminum oxide capacitive sensors in the trace moisture region.

Previously, there was no trace moisture standard, and it was difficult to change the moisture concentration quickly in the trace moisture region. Therefore, there was no method of reliably testing the performance of trace moisture analyzers, particularly in terms of response, but recently, this has become technologically possible owing to the development of the trace moisture standard and trace moisture generation technology.

6 Future developments

Trace moisture measurement traceable to the SI was realized by establishing the national standard, the commercial availability of the CRDS trace moisture analyzer, and organizing the calibration service system. The results of the performance tests presented in chapter 5 clearly show that the reliability of the trace moisture measurement has increased markedly in recent years. However, a CRDS trace moisture analyzer is necessary to perform such measurements, which not all people can easily access because it is an expensive instrument. Therefore, from the perspective of the dissemination of highly reliable trace moisture analyzer, there are still issues concerning the commercial availability of a measuring instrument. To solve these issues, we must wait for the development of low-cost high-performance trace moisture analyzers. Manufacturers are advancing

the research and development of measuring instruments to increase the response of sensors based on the adsorption of water molecules, and some sensors have already been commercialized. Increasing the performance and lowering the cost of these sensors are awaited. For the development of other trace moisture analyzers, a specialized Fourier transform infrared spectrometer (FTIR) for trace moisture measurement has been recently developed and marketed, and the appearance of trace moisture analyzers using absorption spectroscopy techniques other than CRDS is also awaited. In this research, only a few of the conventionally used trace moisture analyzers were tested, and there may be high-performance trace moisture analyzers among those not tested in this research. In order to demonstrate the performance of an instrument, regardless of whether it is a new or conventionally used analyzer, the author considers that it is crucial to carry out performance tests (particularly for response, sensitivity, and drift) using a method traceable to the trace moisture standard. Clearly presenting the test results to other users will lead to the dissemination of a highly reliable trace moisture analyzer.

All the topics in this paper pertain to the trace moisture measurement in nitrogen, but the demand for trace moisture measurement in gases other than nitrogen is increasing in the semiconductor industry. However, there is no trace moisture standard for other gases at present, and it is necessary to consider this issue.

Recently, trace moisture standards have been established in countries other than Japan, and these standards are currently

being developed or maintained by individual countries. In general, the equivalence of national standards maintained by different countries is confirmed through an international comparison. A preliminary international comparison has been initiated recently for the trace moisture standard. Four national metrology institutes, namely, the National Metrology Institute of Japan (NMIJ), National Physical Laboratory (NPL) of UK, National Institute of Standards and Technology (NIST) of the USA, and Physikalisch-Technischen Bundesanstalt (PTB) of Germany, are participating in this international comparison, which is now in progress (as of July 2009). The result will be reported separately. Because an international comparison is extremely important for further increasing the reliability of the AIST trace moisture standard and for its recognition by other countries, we plan to participate actively in such endeavors in the future.

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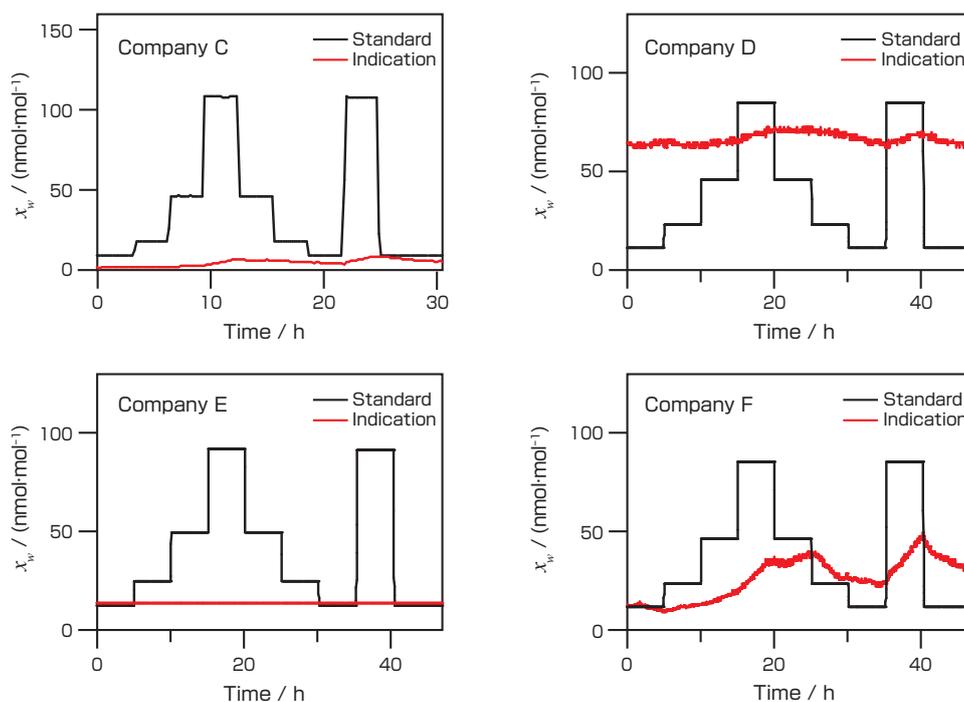


Fig. 15 Comparison of standard value and indication of conventional aluminum oxide capacitive sensor.

Horiba STEC Co., Ltd., and Fujikin Inc., who cooperated in the development and improvement of the instruments. I am also thankful to Mr. Masaaki Maruyama of the Chemicals Evaluation and Research Institute, who helped organize the calibration service system. I thank all those who exchanged opinions about the performance of the conventional trace moisture analyzers.

Terminology

- Term 1. Frost point: The temperature at which condensation occurs when a humid gas is cooled under constant pressure is called the dew point. The dew point is lower when there is less vapor content of the gas. It is called a frost point when frosting occurs below a freezing point.
- Term 2. Primary measurement standard: A standard that is established without relation to a measurement standard of a quantity of the same kind. It has the highest metrological quality and must be given a complete table of uncertainty according to the SI.
- Term 3. Enhancement factor: A coefficient to compensate for the change in vapor pressure caused by the presence of dry air; in the presence of dry air, the vapor pressure obtained is different from that when there is vapor only, because of the additional pressure generated by the dry air, dissolution into water, and interaction with water molecules.

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Discussion with Reviewers

1 Reliability of the vapor pressure equation of ice

Question and comment (Akira Ono, Vice President, AIST)

In many national metrology institutes in countries other than Japan, the national standard for trace moisture is created using the Sonntag's vapor pressure equation for ice. When deriving the Sonntag's equation in the first place, absolute measurements of the trace moisture must have been performed in a manner traceable to the SI. What was the method? Is there an uncertainty attached to the Sonntag's equation?

In this research using a diffusion tube method, the absolute measurement of trace moisture was performed in a manner traceable to the SI. What are the possibilities of investigating the adequacy of Sonntag's equation, or deriving a new vapor pressure equation for ice with an uncertainty using this method?

Answer (Hisashi Abe)

Many of the national metrology institutes other than that in Japan generate a humid gas so that a frost point becomes a set value and constant using a frost point method, and therefore, the traceability to the SI is through temperature. The Sonntag's vapor pressure equation for ice is used when expressing the amount of moisture in a gas as an amount-of-substance fraction and for the calculations when changing the frost point by varying the gas pressure.

The Sonntag's vapor pressure equation for ice was published in Paper [8] in 1990, and this was a recalculation of the existing Wexler's vapor pressure equation for ice (*J. Res. Nat. Bur. Stands.* 1977, vol. 81A, pages 5-20) in accordance with ITS-90, which is the current international temperature scale. Wexler's equation was calculated on the basis of IPTS-68, which was the international practical temperature scale in 1977. Both the Sonntag's and Wexler's equations are obtained by integrating the Clausius-Clapeyron equation. The gas constant and compressibility factor for saturated water vapor over ice needed for the calculation were taken from the values recommended by the Committee on Data for Science and Technology (CODATA) and the values reported in the literature. For details of the calculation, please refer to Wexler's paper.

The relative standard uncertainty of the Sonntag's equation is reported to be less than 0.5 % in the -100 °C to +0.01 °C range^[8]. Comparisons with experimental data have been performed^[9], but relatively large deviations are observed in the trace moisture range (frost point of about -75 °C or less).

The verification of Sonntag's equation is possible to some degree by comparing the experimental results of AIST's diffusion tube method and the experimental results of the frost point method obtained by NPL and NIST through the international comparison

that is currently in progress. This is because, as mentioned above, Sonntag's equation is used when converting the results of the frost point method to the amount-of-substance fraction for comparison. I say "to some degree" here because the verification by this alone is insufficient; the uncertainty of the international comparison (combining the uncertainties of the standards of the two national metrology institutes and the uncertainty caused by the comparison) is larger than the uncertainty of Sonntag's equation in the trace moisture range that requires verification. In this international comparison, we question the validity of Sonntag's equation as a possible factor only when the equivalence of the AIST standard and the NPL or NIST standard cannot be confirmed within the uncertainty.

The derivation of the vapor pressure equation for ice using the diffusion tube method is possible by measuring the frost point of gas generated by the diffusion tube method. However, considering the accuracy of the frost point measurement and the current uncertainty of the diffusion tube method, it is difficult to obtain significant results. I think there is a better possibility of deriving the equation by some other method such as simultaneous measurements of ice temperature and vapor pressure.

2 Calibration for matrix gases other than nitrogen

Question and comment (Akira Ono)

In this research, you established the trace moisture standard by the diffusion tube method using nitrogen as a matrix gas, but what other gases can be used as the matrix gas? For other matrix gases, will it be necessary to individually establish the trace moisture standard using diffusion tube methods? If the standard can be established for one matrix gas (such as nitrogen), can the standard be set easily by relative measurement against other types of matrix gas?

Answer (Hisashi Abe)

In the field of semiconductor manufacturing, matrix gases other than nitrogen that require the trace moisture standards include hydrogen, argon, helium, oxygen, ammonia, and so forth. Although I think it is possible to establish their trace moisture standards and provide a calibration service using the diffusion tube method (although a method must be devised for a gas that is highly soluble in water such as ammonia), it seems not to be highly realistic considering the development cost and user's convenience. Rather, I think it is more realistic to perform a relative measurement to obtain a conversion factor as you mentioned in your question. Please also refer to the second half of the answer to the next question.

3 Use of cavity ring-down spectroscopy for various matrix gases

Question and comment (Akira Ono)

It appears that the absolute values determined using cavity ring-down spectroscopy are consistent with the standard values obtained using the diffusion tube method. Does this mean that the absolute value of the absorption cross section of the water molecule has already been accurately obtained at the wavelength of the laser?

It is mentioned that the absorption cross section is considerably temperature-dependent, but what do you think of the degree of change caused by different matrix gases? If the dependence of the absorption cross section on the matrix gases is small, then can you use the CRDS trace moisture analyzer for measuring trace moisture in other matrix gases if the analyzer was calibrated against a gas generated using the diffusion tube method?

Answer (Hisashi Abe)

A number of studies have reported the line strength of the absorption line monitored in this research used for determining

the water concentration, but there is variation in the values. For example, a difference of approximately 6 % was reported between a value in one study and another value cited in the same study for comparison (*JQSRT* 2005, vol. 94, pages 51-107). Similarly, the maximum difference is 20 % or more in another study (*JQSRT* 2002, vol. 75, pages 493-505). Therefore, rather than already having a sufficiently accurate value, I have an impression that the CRDS trace moisture analyzer used a value which happens to agree relatively well with the standard values. I hope that, by feeding back the results obtained using a method traceable to the SI, the uncertainty of the absorption cross section will be reduced, and the reliability of trace moisture measurement using cavity ring-down spectroscopy will increase further.

The matrix gas dependence of the absorption cross section is not small, for example, there is a twofold difference in values for the absorption line between nitrogen and oxygen (*Appl. Opt.* vol. 44, pages 611-619). However, this relationship can be considered to be almost constant in a small temperature range, and therefore, once the conversion factor is accurately determined at a temperature around which measurement is performed, only the calibration of the instrument for nitrogen will be necessary, and the measurement of trace moisture in oxygen can be performed using the conversion factor. By this method, for matrix gases for which the conversion factor can be obtained with small uncertainty, the reliability of the measurement can be maintained even if there is no trace moisture standard for those matrix gases. Furthermore, the users can skip the calibration for those matrix gases and reduce the management cost. Therefore, I think this is an effective method of trace moisture measurement in gases other than nitrogen. However, when the absorption line of a matrix gas lies in the same wavelength range as the absorption line of water (such as in the case of NH_3), we need to develop an analysis technology to compensate for this effect and to extract information on the moisture concentration. Depending on the type of gas, measurement cannot be performed at all because the absorption of the matrix gas is too strong, and this method may not be effective for all gas types. It is necessary to investigate for which type of gas this method is applicable by considering the uncertainty and the experimental difficulties of determining the conversion factor.

4 National measurement standards and commercially available measuring instruments

Question and comment (Akira Ono)

By using the results of this research, it was clarified that many of the trace moisture analyzers that are already commercially available do not meet the specifications. I think this is an example where a significant social loss may occur owing to the unreliability of commercially available measuring instruments whose measurement capabilities are not adequately demonstrated because of the lack of the corresponding national measurement standard. What lesson should we learn from this?

Answer (Hisashi Abe)

Regarding the conventional commercially available measuring instruments, my understanding is that this situation arose because the instrument manufacturers and retailers endeavored to meet the demands of users who were actually seeking a measurement method of trace moisture, and this situation continued without the national standard for a long time. I think this must be considered as a serious matter, and we must strongly recognize the social importance and impact of standards. Considering the situation of the trace moisture standard of other countries and the period when the CRDS trace moisture analyzer, which was essential for realizing the standard using the diffusion tube method, became commercially available, I think it was technologically difficult to establish the trace moisture

standard before 2001. Ideally, even in such a situation, there should have been a shared awareness among the users, instrument manufacturers and retailers, and researchers of the national metrology institute concerning the technological reasons that prevented the development of the standard and the reliability of the trace moisture measurement without the standard. This is not just the case for trace moisture measurement but can be said to apply to other measurements in a similar situation. How can the three parties share a similar awareness? In particular, this is very difficult to achieve in a situation wherein the researchers have negative opinions (although they are not necessarily correct) about the users' demands. How do we obtain opportunities to publish and discuss such negative matters? It is not easy to bring up negative matters as topics at academic societies and in scientific papers, and even if such a matter is brought up, the probability that this information reaches the users, instrument manufacturers, and retailers is not high. If a technological issue is clarified, it can be published in *Synthesiology* as a research scenario, but even this is difficult without accompanying successful scenarios. One solution is to deepen the understanding of measurement among the users, instrument companies and retailers, and researchers by exchanging opinions using the occasions of visiting the laboratory and by attending the meetings of the Metrology Club organized by the NMIJ. I cannot think of any other particularly effective solution. I am still not fully able to understand what lesson can be learned from this case.

However, concerning the past "social loss" related to trace moisture measurements, I believe the following. Before the trace moisture standard was established, there was no way of objectively investigating the measurement capabilities of trace moisture analyzers, and this fact itself was discovered only after the standard was established. Considering this situation, I think it is a bit too much to say that there was a social loss caused by the unreliable measurements. At the time, no major problems occurred because of the measurements (at least, on the surface), and rather than calling it a social loss, I think we should express it more positively: recently, it has been discovered that there is plenty of room for improvement in trace moisture control in industry.

5 Application of diffusion tube method to organic standard gases

Question and comment (Akira Ono)

In this research, the diffusion tube method was applied to water to generate a standard gas of trace moisture. I think that this method is also applicable to organic substances for the generation of standard gases with a known concentration value. What do you think about this possibility?

Answer (Hisashi Abe)

AIST is the first to succeed in using a diffusion tube method as a primary measurement standard, but this method was originally used as a method for producing a low-concentration standard gas for various substances including organic substances (*Crit. Rev. Anal. Chem.* 2005, vol. 35, pages 31-55). Although there are some limitations, such as it can be used only for substances with a certain degree of vapor pressure at the experimental temperature and for those that do not suffer from the dissolution of the matrix gas, it is generally applicable to substances other than water. In particular, for highly adsorbent substances and those that are unstable and for which long-term storage is difficult, it is difficult to maintain their reliability as a standard gas supplied in a high-pressure container, and the method of continuously generating the standard gas (dynamic method) such as the diffusion tube method is more feasible. The diffusion tube method is introduced in the International Organization for Standardization (ISO 6145-8) as well as in the Japan Industrial Standard (JIS K 0225) as a

simple method to generate a standard gas. However, as found in this research, it should be noted that the reliability of this method in the trace concentration region may not be maintained without using a magnetic suspension balance when the evaporation rate is an extremely small value.

6 Setting goal values for uncertainty

Question and comment (Kazuo Igarashi, Measurement Solution Research Center, AIST)

In chapter 2, you mentioned that the reason for setting 11 % (corresponding to a frost point of 0.5 °C) as the target value of the relative standard uncertainty near the frost point of -100 °C is that the goal of NPL for the standard uncertainty at a frost point of -95 °C was 0.5 °C at the time. The research yielded the excellent result of maintaining the relative combined standard uncertainty at about 3 % by reducing the uncertainties of many components. However, I would like to know the suitability of the 11 % goal because the method of water vapor generation and the accompanying processes were different.

Answer (Hisashi Abe)

Because the significance of selecting the diffusion tube method would be lost if the uncertainty was much greater than that for the frost point method, to begin with we used the target value of the frost point method for the diffusion tube method. Furthermore, we expected that the residual moisture in the zero gas and adsorption/desorption moisture would be major uncertainties in the diffusion tube method, and for the high-performance purifiers used to remove the moisture for zero gas generation, the catalogs from many manufacturers state that the residual moisture is 1 nmol/mol or less. Assuming that the uncertainty caused by the adsorption/desorption of moisture would be at this level, the combined uncertainty of these components would be 1.4 nmol/mol ($\sqrt{1^2 + 1^2} \approx 1.4$), which corresponds to 10 % at 14 nmol/mol. Considering that other components of uncertainty would be included, we did not think at the time that we could achieve the 11 % figure easily. Note that NPL presently sets the lower limit of standard generation by the frost point method to a frost point of -90 °C, and reports that the standard uncertainty at -90 °C is 0.2 °C (about 3.7 %). Therefore, the target value of 0.5 °C for a standard uncertainty at -95 °C initially set by NPL was perhaps slightly too high.

7 Cause of temperature difference in the generation chamber and diffusion cell

Question and comment (Kazuo Igarashi)

The evaluation of uncertainty is performed in section 3.3, and you mention that it arises from the difference between the temperature of water inside the generation chamber and the diffusion cell. It seems that the reasons for the temperature difference may be attributable to the temperature control depending on the flow rate of the nitrogen gas and the low heat conductivity of the SUS stainless steel used as material of

the diffusion cell. If you have considered these factors, please describe them, as it will be of use in detailed investigations.

Answer (Hisashi Abe)

I added the assumption of the factors that produced the temperature difference to the text. Investigating the reasons why the room temperature change affects the measurement results is an important issue when considering the validity of the evaluated uncertainty, or the uncertainty of the uncertainty (here, this means the uncertainty of the sensitivity coefficient determined by experiment). However, we have not yet performed experiments regarding this issue or to investigate the flow rate dependence as you indicated, so the clear reason is still unknown. However, for the uncertainty of the sensitivity coefficient, from the discussions in Ref. [23], I do not think that it is particularly large under the current experimental conditions. If the obtained sensitivity coefficient is correct, reducing the uncertainty caused by the change in room temperature is not difficult compared with reducing the uncertainties of other components at this stage, and therefore, we have not performed any additional investigation of the reasons for the cause of the temperature difference.

8 Effect of purity of water

Question and comment (Kazuo Igarashi)

In generating trace water vapor, you analyzed several factors such as the adsorption/desorption of moisture, residual moisture in the zero gas, and the gas flow meter, but you do not refer to the purity of water itself. Is this because you think that it is not a problem as long as the purity level does not affect the vapor pressure?

Answer (Hisashi Abe)

I often receive questions regarding the purity of water, but I did not discuss this in the text because of the space limitation of the journal, so I shall explain it here. In this research, we used highly purified water obtained from an ultrapure water production system. However, the purity of water itself is not a major issue. This is because the evaporation rate is measured as the mass change of the diffusion cell per unit time, and therefore, even if there is an impurity in the water, it will not be an issue as long as it remains in the diffusion cell. If a gas is dissolved in the water, it may become a factor of uncertainty because it evaporates with water, but such a gas is probably removed by the aforementioned ultrapure water production system, and I think that the effect can be ignored. Furthermore, the measurements are performed after placing the diffusion tube inside the generation chamber into which highly pure nitrogen is introduced for a sufficiently long time (normally 10 days or more). Therefore, even if there is a residual gas, it will be replaced by nitrogen. Finally, for the nitrogen dissolved in water, even if it is saturated at a pressure of 150 kPa and a temperature of 25 °C inside the generation chamber, its amount-of-substance fraction is 0.002 % or less, which can be ignored in this research.