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Trace-moisture generator designed for performance tests of trace-moisture analyzers

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ABSTRACT

The National Metrology Institute of Japan (NMIJ) developed a trace-moisture generator, named the "simplified trace-moisture generator (STMG)," which was designed particularly for effectively testing the performance of trace-moisture analyzers. The STMG produces trace moisture in nitrogen gas from approximately 10 nmol/mol (ppb) to 10 μmol/mol (ppm) in amount fraction (mole fraction) of water, using diffusion-tube and two-stage dilution methods. In contrast to the magnetic suspension balance/diffusion-tube humidity generator (MSB/DTG) developed at NMIJ in 2007, the STMG does not require an MSB to measure the evaporation rate of water from the diffusion cell (hence, the name "simplified"). Instead, a moisture analyzer based on cavity ring-down spectroscopy (CRDS) calibrated in a manner traceable to the International System of Units (SI) measures the amount fraction of water in the generated gas. By introducing a sonic nozzle placed at the outlet of the generation chamber, the pressure stability in the chamber is maintained even after the rapid change in the flow rate of the diluent nitrogen gas. This enabled smooth moisture-concentration switching within 1 min for 90 % response to the step change between 11 nmol/mol and 8.8 μmol/mol. The controllability and short-term stability of the moisture content in the generated gas were demonstrated successfully. The long-term stability of moisture generation was evaluated by estimating evaporation rate from the flow rate of nitrogen and the amount fraction of water measured by the CRDS trace-moisture analyzer. It was confirmed that the STMG can generate trace moisture in nitrogen with good stability and repeatability for five consecutive months.

1. Introduction

The measurement of trace water vapor (trace moisture) in a gas, even when present at amount fractions (mole fractions) less than 1 μmol/mol (ppm), is crucial in the manufacture and design of various cutting-edge products. For example, moisture control is essential in the process gases used for semiconductor manufacturing [1,2] and moisture measurement is applied to the evaluation of the water barrier properties of high-barrier transparent films used for sealing flexible organic light-emitting diode devices [3] or organic solar cells [4]. Trace-moisture analyzers based on various principles have been used in those processes. To obtain reliable measurement results, the characteristics and behavior of the trace-moisture analyzers have to be properly understood. However, primary trace-moisture standards less than 1 μmol/mol were not available until only some years ago, and, therefore, trace-moisture analyzers have been neither calibrated nor tested with metrological traceability to the International System of Units (SI). That is, trace-moisture analyzers have had little calibration and testing to assure the reliability of measurement results.

The National Metrology Institute of Japan (NMIJ) developed a magnetic suspension balance/diffusion-tube humidity generator (MSB/DTG) [5] and launched a calibration service for trace-moisture in nitrogen gas in the range from 12 nmol/mol (ppb) to 1.4 μmol/mol [6]. Using the MSB/DTG, the measurement capabilities of the conventionally used trace-moisture analyzers were also tested. The results suggested that many commonly used trace-moisture analyzers do not have a sufficient measurement capability at or below 1 μmol/mol [6], indicating that the improvement and development of trace-moisture analyzers is urgently needed. The performance evaluation of the trace-moisture analyzers is essential to achieving success in such improvement and development. An important characteristic of trace-moisture analyzers to be evaluated is their response to step changes in moisture content. However, the testing of the response of trace-moisture analyzers is intrinsically difficult because accurately and rapidly changing the moisture to a target value is difficult in the trace-moisture region. Using the MSB/DTG, such testing is possible. However, the

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Table 1
Comparison of characteristics of the MSB/DTG and STMG.

	MSB/DTG	STMG
Classification of standard	Primary measurement standard	Secondary measurement standard
Dilution method	Single dilution	Two-stage dilution
Generation range	12 nmol/mol–1.4 μmol/mol	10 nmol/mol–10 μmol/mol
Maximum dilution	1/20	1/1000
Flow rate capacity	1 L/min (at 1.4 μmol/mol)	4 L/min (at 10 μmol/mol)
Gas outlet for the DUT(s)	Single outlet	Four outlets
Time required for change	≥10 min (12 nmol/mol–240 nmol/mol)	<1 min[a] (11 nmol/mol–8.8 μmol/mol)

[a] 90 % response time.

MSB/DTG was originally developed for use in calibration, and therefore, has the following disadvantages when it is used for testing the response: a wide generation range is not possible, only one analyzer can be tested at a time, and the rate of change in moisture content is limited. In this study, a new trace-moisture generator was developed to overcome these disadvantages. It was named the "simplified trace-moisture generator (STMG)," because it does not require the MSB to determine the amount fraction of water in the generated gas; instead, the values obtained using a calibrated trace-moisture analyzer based on cavity ring-down spectroscopy (CRDS) [7–10] are used as trace-moisture standards, enabling a markedly simplified system configuration compared with that of the MSB/DTG. To establish a measurement standard with MSB/DTG, it was indispensable to develop a system for measuring evaporation and flow rates in a manner traceable to the SI and to evaluate uncertainties in their measurement results. The amount of residual moisture in dry gas and its effect on uncertainty should also be evaluated. The details of the development of the MSB/DTG and the uncertainty analysis were reported elsewhere [6]. However, in the STMG, many of these complex tasks are unnecessary as the operating principle and uncertainty analysis for the measurement results are much simpler than those in the MSB/DTG.

2. Design principles

Here, the design principles of the STMG are described in comparison with those of the MSB/DTG, as summarized in Table 1. Both the MSB/DTG and the STMG use diffusion cells as sources of trace moisture. The MSB/DTG determines the amount fraction of water in the generated gas from the measurement of evaporation and flow rates, whereas the STMG determines it from the measurement of the amount fraction of water using a CRDS-based trace-moisture analyzer that is calibrated using primary measurement standards. According to the International Vocabulary of Metrology [11], a primary measurement standard is defined as a measurement standard established using a procedure with which a measurement result can be obtained without relation to another measurement standard for a quantity of the same kind, and a measurement standard established through calibration with respect to a primary measurement standard for a quantity of the same kind is classified as a secondary measurement standard. Hence, the MSB/DTG and STMG are facilities for a primary measurement standard and a secondary measurement standard, respectively.

The MSB/DTG can achieve only a 1/20 dilution using a single dilution system. For this reason, the MSB/DTG has to change the temperature of the generation chamber to cover the range of 12 nmol/mol–1.4 μmol/mol; setting temperatures of 25 °C and 60 °C are used for the ranges of 12 nmol/mol–240 nmol/mol and 70 nmol/mol–1.4 μmol/mol, respectively, where 60 °C is the maximum setting temperature. The STMG adopts a two-stage dilution system using three thermal mass flow controllers (MFCs), two of which are used for dry gas inputs and the other of which is for exhaust, making it possible to achieve an approximately 1/1000 dilution. The amount fraction of water in the generated gas is expected to be variable from 10 nmol/mol to 10 μmol/mol without changing the temperature of the generation chamber to change the evaporation rate.

The flow rate of the generated gas usable for testing or calibrating devices under test (DUTs) decreases with increasing amount fraction of water in the gas. The MSB/DTG can produce a gas at 1.4 μmol/mol only with a flow rate up to 1 L/min (volume flow rate under the standard condition of 101.325 kPa and 0 °C is used to express flow rate in this paper; 1.00 L/min corresponds to a mass flow rate of 1.25 g/min for nitrogen gas). In contrast, the maximum flow rate obtainable for the STMG at 10 μmol/mol is approximately 4 L/min, which is sufficient for accepting one CRDS-based trace-moisture analyzer used to determine the amount fraction of water in the gas generated and four trace-moisture analyzers to be tested at a time.

The amount fraction of water was changed by changing the flow rate of dry gas in the MSB/DTG. When the flow rate was very rapidly changed, a marked pressure variation was observed in the generation chamber, leading to unstable moisture generation. In general, therefore, the rate of change in flow rate was limited in a generator that uses a diffusion-tube method. The time required for the change between 1 L/min and 20 L/min, corresponding to the trace-moisture generation of 12 nmol/mol and 240 nmol/mol, respectively, was 10 min in the MSB/DTG. Considering the additional time required for the replacement of the gas in the line and the state of equilibrium to be achieved, it must be greater than or equal to 10 min for the change between 12 nmol/mol and 240 nmol/mol. In the STMG, a critical flow Venturi nozzle (sonic nozzle) is installed at the outlet of the generation chamber to suppress the pressure variation and allow us to rapidly change the flow rate. The sonic nozzle can isolate the generation chamber from the dilution system in terms of the pressure variation when the ratio of the pressure downstream of the nozzle P_2 to the pressure upstream of the nozzle P_1 is reduced to less than the critical pressure ratio ($P_2/P_1 = 0.53$). Under this condition, the gas flow velocity at the nozzle throat becomes constant (speed of sound), and the disturbance of P_2 is not transmitted to P_1. Therefore, a rapid change in flow rate is possible without causing the moisture generation from the diffusion cell to be unstable. In this case, the time required for the change in moisture content in the gas generated is limited only by the response time of the CRDS-based trace-moisture analyzers. The 90 % response time between 11 nmol/mol and 8.8 μmol/mol was less than 1 min, as demonstrated in Section 4.2.

3. Experimental setup

Fig. 1 shows the experimental setup based on the design principles described in Section 2. In this study, we used a diffusion cell consisting of a diffusion tube (4.4 mm internal diameter and 30 mm length) and a cylindrical water vessel (20 mm internal diameter and 80 mm depth), both of which are made of SUS316L stainless steel. The diffusion tube was removable from the vessel with a screw to pour water into the vessel. The generation chamber was cylindrical with an internal diameter of 40 mm and a length of