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A round-robin test of thermal desorption spectroscopy with quadrupole mass spectrometers calibrated by standard conductance element

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ABSTRACT

The results of a round-robin test of thermal desorption spectroscopy (TDS) in which the quadrupole mass spectrometer of each participant was calibrated in-situ by a standard conductance element are reported. The desorption rate from three commercially available reference materials was quantified from the calibration results, and compared among the three participants. The total reported desorption amounts of hydrogen and argon molecules from the reference materials showed agreement within about 10%. The degree of equivalence of three TDS apparatuses was discussed. It is also shown that the quantification of the gas desorption amounts yields us the appropriate relative ratio between desorbed gas species.

1. Introduction

Thermal desorption spectroscopy (TDS), which has developed in 1960s [1–5], is a widely used basic analytic technique for vacuum materials. For TDS analyses, a sample is heated with a constant ramp rate in the vacuum chamber. The types and the desorption rate of gases from the sample are measured by a quadrupole mass spectrometer (QMS). The activation energy for desorption is also calculated from the desorption temperature by assuming an appropriate model.

A calibration of the QMS enables quantitative evaluation of gas desorption rates. Quantitative measurements of the gas desorption rate are increasingly necessary to obtain clean vacuum, which is used in various applications such as semiconductor manufacturing, coating, display production, accelerators, and nuclear fusion [6,7], as well was being used to evaluate hydrogen degradation in steel [8,9]. A few reports of round-robin tests of TDS have been previously published. Behrisch et al. [10] compared the amounts of deuterium atoms in carbon/silicon as measured by MeV ion beam analysis, secondary ion mass spectrometry (SIMS), and TDS among 6 participants. Suzuki and Takai [8] compared the hydrogen concentration in steel as measured by gas chromatography and TDS among 21 institutions. Although these results agree within several tens of percent, little information on the calibration of QMSs is described.

We have developed a leak element, a sintered stainless steel filter with a pore size of less than 1 μm, which is known as a “standard conductance element (SCE)” [11–14], for in-situ calibration of QMSs by using various gas species. A round-robin test of TDS, for which the QMS of each participant was calibrated in-situ by an SCE, was performed to confirm the compatibility of measurement results obtained by different apparatuses. Three testing laboratories participated in this round-robin test. Different types of QMSs, different heating systems with different applicable ramp rates,

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turbomolecular pumps (TMPs) with different pumping speeds, and different configurations of vacuum chamber are employed in their TDS apparatuses. Despite such differences, total desorption amounts of gas molecules from a sample should be comparable after correcting raw data with the results of in-situ calibration. It is impossible, however, to exactly reconcile the total desorption amounts obtained by different apparatuses because both in-situ calibration and TDS measurement have inherent uncertainty. The purpose of this round-robin test is to examine to what degree the in-situ calibration of QMSs by SCE normalizes the total desorption amount of gas molecules measured by different TDS apparatuses.

2. Principle of quantitative measurement of gas desorption rate by TDS

Gas desorption rate q_i for gas species i from a sample is equal to Eq. (1)

$$q_i = S_{\text{eff-}i} \cdot (p_i - p_{i0}) + V \cdot \left(\frac{d(p_i - p_{i0})}{dt} \right), \tag{1}$$

where $S_{\text{eff-}i}$, p_i, p_{i0}, V, and t is the effective pumping speed of the vacuum pump for gas species i, the partial pressure of gas species i, the background of the partial pressure of gas species i, the volume of the vacuum chamber, and time, respectively [1–5]. When $S_{\text{eff-}i}$ is selected so that the first term on the right-hand side is much larger than the second one, Eq. (1) is rewritten as (2).

$$q_i = S_{\text{eff-}i} \cdot (p_i - p_{i0}). \tag{2}$$

The sensitivity K_i of QMS for gas species i is shown by the equation,

$$K_i = \frac{I_i - I_{i0}}{p_i - p_{i0}}, \tag{3}$$

where I_i and I_{i0} are the ion current at the main peak for gas species i during TDS analysis and at background, respectively. Eq. (4) is obtained by substituting Eq. (3) into Eq. (2),

$$q_i = \frac{S_{\text{eff-}i} \cdot (I_i - I_{i0})}{K_i} = \frac{I_i - I_{i0}}{S_{qi}}, \tag{4}$$

where S_{qi} is defined as the flow sensitivity [15] for gas species i. Note that the S_{qi} has the gas species dependence because both $S_{\text{eff-}i}$ and K_i depend on the gas species.

Gas molecules on the sample surface are desorbed at the temperature which is mainly determined by the activation energy for desorption. Since the sample is heated with a constant ramp rate for TDS, gas desorption rate q_i changes depending on time. The total desorption amount Q_i of the desorbed gas is obtained by the time integration of Eq. (4),

$$Q_i = \frac{1}{S_{qi}} \int (I_i - I_{i0}) dt \tag{5}$$

Here, S_{qi} is assumed to be independent of the pressure. When a sample is heated with a constant ramp rate α, Eq. (5) is rewritten as Eq. (6) because $T_s = \alpha t + T_0$ where T_s and T_0 (constant) are sample temperature during heating and just before heating, respectively,

$$Q_i = \frac{1}{S_{qi} \cdot \alpha} \int (I_i - I_{i0}) dT_S. \tag{6}$$

Quantitative measurements of gas desorption rate are achieved by determining both $S_{\text{eff-}i}$ and K_i, in other words, S_{qi}. There are two methods to determine S_{qi}. One is that S_{qi} is calculated from K_i and $S_{\text{eff-}i}$ which are individually measured, and the other is that S_{qi} is directly calibrated by introducing a reference leak. The latter one is adopted in this study.

The various units of desorption rate are used depending on the purpose and the fields, e.g. Pa m^3/s, mol/s, g/s, molec./s, and so on. These units are converted to one another by using an equation of state of an ideal gas, although the chamber temperature is necessary for the unit conversion of Pa m^3/s. An unit of molec./s is used in this study.

3. Experimental

3.1. Apparatuses and results of in-situ calibration of QMSs

The test period, the heating condition, the nominal pumping speed of the TMP for N_2, and the condition and results of in-situ calibration are summarized in Table 1 for three participants. Typical chamber temperatures were 25.8 °C for participant A, 25.1 °C for B, and 23.6 °C for C, respectively.

Participant A heated samples by irradiating infrared rays from below. Participants B and C introduced samples into an electric furnace and an infrared image furnace, respectively, and heated samples. Ramp rates were adopted from their typical procedure. Participants A and B heated samples to 1200 °C and 1000 °C, respectively, which were considered sufficient to desorb target molecules from test samples on the basis of previous studies [8,9,16,17]. Although the maximum temperature of participant C was 750 °C, participant C held the temperature at 750 °C for 1 h to desorb the gas molecules entirely.

The TMPs of participants A and B are directly attached to their vacuum chambers. For participant C, an orifice with a diameter of 15 mm is in front of its TMP. The maximum ratio between nominal pumping speeds of the pumping systems is about 100.

Each participant employs a QMS from a different manufacturer. Operating parameters of the QMSs were adopted from typical values of their daily measurement. The secondary electron multiplier was applied for all participants. Fig. 1 shows a schematic diagram of the in-situ calibration system with a SCE attached to the vacuum chamber of the TDS apparatus. In the system, a reference leak is introduced from the gas reservoir to the vacuum chamber through the SCE to calibrate QMS. The pressure in the gas reservoir is limited up to 10 kPa so that the gas flow through the SCE satisfies the molecular flow condition. The flow rate q of the reference leak is calculated from the molecular conductance of the SCE, the pressure in the gas reservoir, and the temperature. All participants calibrated their QMSs for H_2, N_2, and Ar by use of an SCE whose molecular conductances for N_2 were calibrated at the National Metrology Institute of Japan (NMIJ). Operating