Adsorption 11: 227–230, 2005

High Precision Volumetric Gas Adsorption Apparatus

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Abstract. We have developed a new volumetric gas adsorption apparatus into which the dead volume measurement cell (dVd cell) is incorporated (cf. Fig. 1). The dVd cell measures continuously the change of dead volume during adsorption measurement. The dead volume at every step of adsorption measurement is used in calculation of adsorbed amount of nitrogen gas. Introduction of the dVd cell makes the level-control system of liquid nitrogen unnecessary, and enables the adsorption error due to the minute fluctuation of liquid–nitrogen level small. The sensitivity and reproducibility of our new adsorption apparatus have been examined using some certified materials (cf. Fig. 4).

Keywords: volumetric method, continuous dead volume measurement, high reproducibility, surface area

1. Introduction

Adsorption-desorption isotherms of nitrogen at its boiling point (77 K) have been widely used to calculate surface area and porosity of various materials. The volumetric gas adsorption apparatus is useful to measure the nitrogen isotherms. In order to calculate specific surface area with high accuracy and high reproducibility, adsorption isotherms must be measured accurately. In the volumetric method, the amount of adsorption is calculated from state equation of gas (pressure, temperature and volume) and there are a variety of error sources such as dosing volumes, temperature and pressure measurement, sample mass measurements and so on. The estimation of dead volume (*Vd*), free space in the sample container, is important for calculation of adsorption amount in volumetric method. But it is difficult to know the correct *Vd*. One way to determine *Vd* is to measure it before or after the measurement using helium at the measuring temperature and amount of adsorption is calculated under assumption that the *Vd* value is constant during the adsorption measurement. In this case, *Vd* should be kept constant. In another way, *Vd* has to be compensated continuously. There are various ways to determine the *Vd* value. For example:

(i) Isothermal jacket method. (Porous material tube)
(ii) Dewar elevator method
(iii) Vacuum jacket method. (Vacuum sealed sample cell)
(iv) LN_2 transfer method
(v) Pre-measurement method. (Blank measurement)

In those methods from (i) to (iv), the liquid nitrogen level in the dewar vessel (LN_2 level) should be kept constant. Various efforts have been made to maintain liquid nitrogen level (Naono and Nakai, 1989). But it is not easy to maintain LN_2 level without any fluctuations. In addition to that, not only LN_2 level fluctuations but also other factors (room temperature, atmospheric pressure and slight dissolution of oxygen into LN_2) cause change of *Vd*. To keep *Vd* value completely constant is quite difficult.

In the method (v), a blank measurement has to be carried out in advance and an isotherm should be measured at the same condition as the blank isotherm is measured. Because all the conditions are not absolutely same in *Vd* measurement and in adsorption measurement, to measure *Vd* change beforehand is not enough correct. We propose a new method to measure *Vd* with a fair

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degree of precision without controlling LN_2 level. This method is effective especially in measurement of small surface area sample and reproducibility improves.

2. Principle of Continuous Dead Volume Measurement

During the adsorption measurement, LN_2 level goes down gradually by evaporation and as a result, *Vd* gradually decreases. We adopt dVd cell to calculate how much the *Vd* changes are (see Fig. 1). The dVd cell consists of a cell which has the same inner diameter as the sample cell and a pressure transducer. Prior to the adsorption measurement, a certain amount of helium gas is enclosed into dVd cell. Then immerse both cells into LN_2. The dead volume of the sample cell is defined as $Vd_{\mathrm{smp}}(n)$. In the same way, the dead volume of dVd cell is defined as $Vd_{\mathrm{ddVd}}(n)$ and the pressure inside dVd cell is defined as $P_{\mathrm{dVd}}(n)$. The number in parentheses indicates the LN_2 level (Level-1 or Level-2).

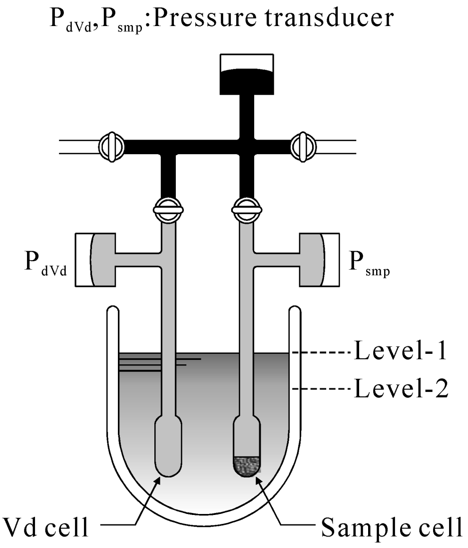

Figure 1. Continuous dead volume measurement.

$Vd_{\mathrm{dVd}}(2)$ is expressed as follows.

$$Vd_{\mathrm{dVd}}(2) = Vd_{\mathrm{dVd}}(1) \times P_{\mathrm{dVd}}(1)/P_{\mathrm{dVd}}(2) \qquad (1)$$

The variation in Vd_{dVd} when the LN_2 level goes down from Level-1 to Level-2 (ΔVd_{dvd}) is expressed as follows.

$$\Delta Vd_{\mathrm{dVd}} = Vd_{\mathrm{dVd}}(2) - Vd_{\mathrm{dVd}}(1) \qquad (2)$$

Because the inner diameters of dVd cell and the sample cell are the same, V_{dsmp} change equals to ΔVd_{dvd}. As a result $Vd_{\mathrm{smp}}(2)$ is expressed as follows.

$$\begin{aligned} Vd_{\mathrm{smp}}(2) &= Vd_{\mathrm{smp}}(1) + \Delta Vd_{\mathrm{smp}} \\ &= Vd_{\mathrm{smp}}(1) + \Delta Vd_{\mathrm{dVd}} \qquad (3) \end{aligned}$$

With our new method (continuous dead volume measurement system), LN_2 level control is not necessary, which leads to a trouble free system and cost savings. Furthermore, *Vd* is compensated at every step of adsorption measurement precisely, which makes it possible to measure adsorption isotherms with high accuracy and reproducibility. This system is effective especially in measurement of low surface area material.

3. Results and Discussions

Figure 2 shows the pressure transition of dVd cell and the changes in dead volume calculated from it. In the following calculation, we use sample cell that has inner

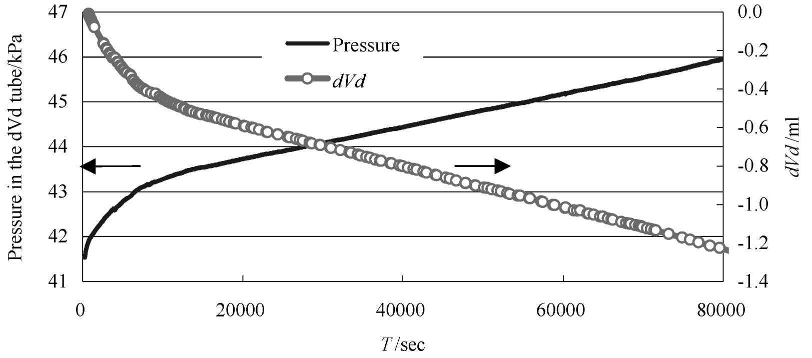

Figure 2. Transition of *Vd*.

diameter of 7 mm with filler rod of 6 mm in diameter to reduce dead volume. Given that LN_2 level is kept to be constant within 1 mm, the dead volume error is estimated to 0.073 ml. It causes 0.12 m^2 of uncertainty in the total surface area calculation. As is described previously, the dead volume uncertainty depends on a variety of factors; hence the surface area error should be considered to be bigger than we calculated.

We developed a new adsorption apparatus, BELSORP-mini, which adopts the continuous dead volume measurement system. We measured isotherms of two certified materials.

(1) LGC2102

- Nonporous graphitised carbon black.
- Certified value of nitrogen BET specific surface area is 69 ± 2 m^2 g^{-1}
- Supplied by LGC in UK.

(2) CRM-170

- Nonporous alpha alumina
- Certified value of nitrogen BET specific surface area is 1.05 ± 0.05 m^2 g^{-1}
- Supplied by BCR in UK.

Five isotherms of LGC2102 measured with BELSORP-mini are shown all together in Fig. 3. They coincide well in the whole relative pressure range. As is often the case, measurable lower limitation of specific surface area is described to express the specification of an adsorption apparatus but we believe it is not enough.

Table 1. Total surface area and measuring error.

Sample	LGC2102				CRM-170			
Total surface area/ m^2	35.2	14.0	7.09	3.94	0.98	0.75	0.12	0.022
No. of measurement	5	5	5	5	10	5	10	9
Error (%)	0.05	0.30	0.33	0.59	1.3	1.77	6.9	36.4

We make a suggestion that reproducibility against the total surface area should be represented for the purpose. We measured adsorption isotherms of LGC2102 and CRM-170 for estimation of reproducibility. Adsorption isotherms are measured in different total surface area. These measurements were carried out with using the same sample and the same sample cell repeatedly to avoid the sample weighing error. The total surface area and the reproducibility are shown in Table 1 and Fig. 4. In general, it becomes more difficult to measure nitrogen isotherms on low-area adsorbents (if the specific surface area <5 m^2 g^{-1}) in conventional methods (Rouquerol et al., 1999). However our new method makes it possible to measure low uptakes of gas with high reproducibility (when total surface area >1 m^2 g^{-1}, measuring error $<1.3\%$).

Isotherms of LGC2102 in the relative pressure range from 0.9 to 1.0 are displayed on the right in Fig. 3. Adsorbed amount are represented as the liquid volume of nitrogen. As we described before, the isotherms coincide well even in the high relative pressure range. It means that the reproducibility of the pore volume is high as well as the specific surface area. According

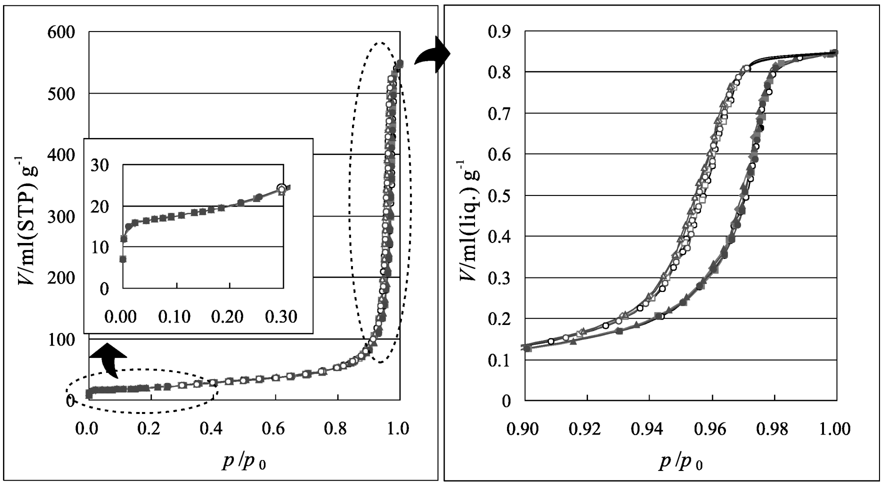

Figure 3. Adsorption isotherms of LGC2102.

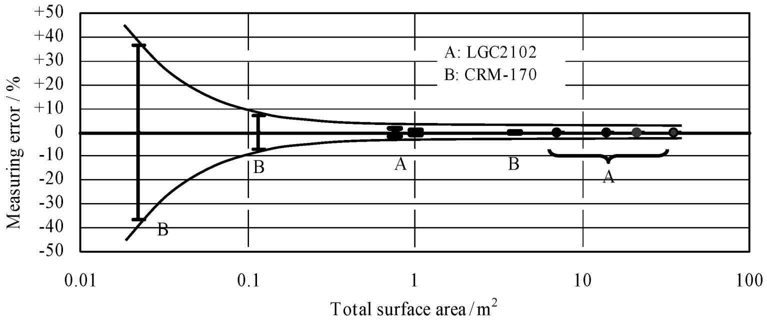

Figure 4. Reproducibility against total surface area.

to Gurvitsch rule, the pore volume of LGC2102 (at $p/p^0 = 0.99$, pore radius <93 nm) was estimated to 0.83 cm^3 g^{-1} with STD of 0.003 cm^3 g^{-1}. This high reproducibility in high rerative pressure range indicates a possibility for analyzing macropore by gas adsorption.

Measuring error is calculated as follows.

$$\text{Measuring error}(\%) = \pm(\text{Sandard deviaton})/(\text{Average of total surface area}) \tag{4}$$

4. Conclusions

In the conventional volumetric method, determining dead volume is quite difficult. Precise LN$_2$ level control is necessary in some of them. When measuring low surface area material, using krypton gas is desirable instead of nitrogen gas for operational reason. But in using krypton gas, high vacuum system is needed and there are some technical problems.

Comparing to these conventional methods, our new volumetric method;

1. Does not need to maintain LN$_2$ level.
2. Improves reproducibility both in surface area and in pore volume.
3. Makes it possible to measure adsorption isotherm of low surface area material (e.g. 0.1 m^2 in total surface area) without using krypton gas.

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