Thermochimica Acta, 103 (1986) 89–96
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

QUASI-EQUILIBRIUM NITROGEN ADSORPTION GRAVIMETRY : COMPARISON WITH VOLUMETRY FOR THE DETERMINATION OF SURFACE AREAS AND PORE SIZE DISTRIBUTIONS

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ABSTRACT

The comparison involves one gravimetric technique and two volumetric ones (either conventional or quasi-static). The samples used are a bronze powder (0.1 m^2g^{-1} only), a graphite powder (*c.a.* 10 m^2g^{-1}, with a phase change of the nitrogen monolayer used as a sensitive thermometer) and two mesoporous silica gels (pore size *c.a.* 5.0 and 11.5 nm). Relative advantages of either technique are pointed out.

INTRODUCTION

When the problem of selecting a nitrogen adsorption equipment occurs, one of the first choices to be done is between a *gravimetric* and a *volumetric* method. The comparison has often been carried out but, because of the variety of equipment and experimental procedures available in either method, general conclusions are necessarily either vague or, if more precise, somewhat biased (especially if a sophisticated equipment of one method is compared with a trivial one of the other!).

This is why we found it useful to limit ourselves to *three equipment and experimental procedures* (one gravimetric and two volumetric) among those we have been using for the last 10 years (so that we don't claim for general conclusions) and to stay within the scope of *nitrogen* adsorption to determine *specific surface areas* and *pore size distributions*. A useful document, in this respect, will be the recent IUPAC recommendation on "Reporting physisorption data for gas/solid systems, with special reference to the determination of surface area and porosity" (ref. 1).

EXPERIMENTALS

The three techniques under comparison are the following :

o *quasi-static adsorption gravimetry*, which was described previously (ref. 2) and whose main features are (i) the use of a symmetrical beam vacuum microbalance (Setaram MTB 10-8) (ii) the slow and *continuous introduction of adsorptive* in quasi-equilibrium conditions (typically, 2 to 15 hours to complete the adsorption

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isotherm up to saturation)(iii) the *automatic recording of the adsorption-desorption isotherm* on a XY recorder (the adsorbate uptake *i.e.* the mass signal, is recorded *vs* the pressure signal from a Texas gauge) and (iv) the automatic control of the pressure and rate of preliminary *in situ* outgassing following the principle of Controlled outgassing Rate Thermal Analysis (CRTA (ref. 3 , 4)). This equipment can also be used with an automatic point-by-point procedure but one then loses the most interesting possibility (especially from the point of view of resolution) of getting an infinity of experimental points from a single experiment. For this reason, we shall only report on the quasi-static use of adsorption gravimetry;

o *quasi-static adsorption volumetry* (ref. 5 , 6) which is still simpler, since here only the quasi-equilibrium pressure (measured with a Barocel or Baratron capacitance manometer) needs to be recorded *vs* time. This is made possible because the introduction of adsorptive is not only slow and continuous (like in quasi-equilibrium adsorption gravimetry) but is also at *constant flow rate*. This condition can be fulfilled up to a quasi-equilibrium pressure of *c.a.* 300 torr which, in the case of nitrogen adsorption at 77 K (only considered here) allows to obtain the full BET region of the isotherm but not the hysteresis region. The conditions in which this quasi-static procedure is valid were determined by comparison with conventional point-by-point adsorption volumetry (ref. 5);

o *conventional adsorption volumetry* with mercury burets and manometer enclosed in a thermostated cabinet. The equipment is the one described in (ref. 7). It only lends itself to the point-by-point procedure but allows to obtain the complete adsorption-desorption isotherm, so that it complements the quasi-static volumetric apparatus. Since it is based on the principle of a step-by-step compression of the starting amount of gas, its accuracy, at any time, does not depend on the number of previous equilibrium points. Contrary to the two techniques mentioned before, this one is not automatic.

We may point out that, in the case of adsorption volumetry (by either technique) preliminary outgassing was carried out by attaching the adsorption bulbs to a special equipment applying the same CRTA principle as used in the gravimetric equipment. Finally, the three techniques were used with the same type of liquid nitrogen bath (level control within ± 0.5 mm and internal supply of liquid nitrogen to minimize both thermal disturbances and nitrogen consumption (ref. 2 , 5).

Four samples were chosen for their characteristic adsorbent properties :

o A *bronze powder* of *c.a.* 0.1 m^2g^{-1} which is, as we shall see, in the range of the smallest specific surface areas which may presently be determined by nitrogen adsorption. This sample is currently being characterized as a *surface* *area* reference material in the scope of the Bureau Communautaire de Référence in Brussels*

o A *graphite powder* (Sterling FT-G carbon black from Cabot, graphitized at 2700°C (ref. 8)) with a specific surface area of *c.a.* 10 m^2g^{-1} and which gives rise to a typical sub-step of the nitrogen adsorption isotherm (near the completion of the monolayer) which we could interpret as being due to a transition from a 2D hypercritical fluid to a 2D solid (ref. 9)

o Two mesoporous precipitated silica-gels with "nominal" pore diameters of 5.0 nm and 11.5 nm which have been considered, at a time, as potential *pore size* reference materials by BCR.

RESULTS AND DISCUSSION

Surface area

To compare quasi-static adsorption gravimetry with quasi-static adsorption volumetry we may look at the four parameters needed for the calculation of the BET surface area :

Amount adsorbed. Fig. 1 shows, for the bronze sample, in the BET pressure region, the nitrogen adsorption isotherm as directly recorded in about 2 hours by quasi-static adsorption gravimetry. Although a specific surface area of

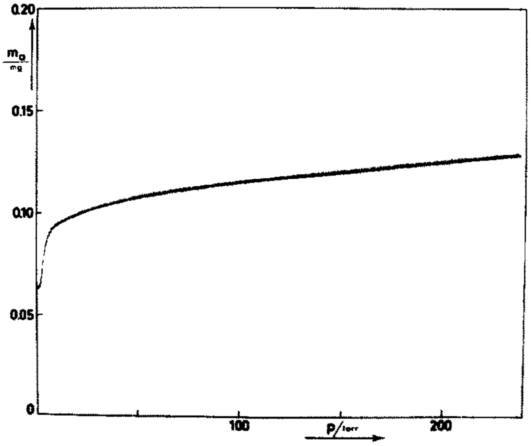

Fig. 1. Adsorption isotherm of nitrogen on bronze (0.1 m^2g^{-1}) at 77K (direct gravimetric recording).

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* This BCR working group presently includes five European laboratories : D.H. Everett (Bristol) and R. Wilson (NPL, Teddington) in U.K. ; K. Unger (Mainz) in Germany, N. Pernicone (Novara) in Italy and ourselves in France.

0.1 m^2g^{-1} is generally considered as too small to be determined by nitrogen adsorption, one sees that this recording, obtained with a 5g sample (the maximum load of our equipment being *c.a.* 6g), is still quite satisfactory. A similar recording may be obtained by quasi-static adsorption volumetry but it needs a sample mass (and therefore an adsorption time to stay in quasi-equilibrium conditions) about twice larger. In other words, the sensitivity of the quasi-static gravimetric technique used here is presently *c.a.* twice higher than that of the quasi-static volumetric technique. The question of the buoyancy correction (for gravimetry) and of the void volume correction (for volumetry) has of course to be considered here. As pointed out by Everett (ref. 10) and by Fuller et al. (ref. 11) both corrections are identical. We may say that, in terms of the amount adsorbed, they are *both equal to the amount of adsorptive excluded by the volume of adsorbent.* They both suffer from the *same uncertainty* on the determination of the "volume of adsorbent" with a gas which is supposed not to be adsorbed and supposed to reach the same pores as the adsorbate. *This uncertainty is not cancelled nor even minimized by a mechanical compensation of the buoyancy effect,* although this allows to increase the relative accuracy of the mass change recording. Let us finally point out that, contrary to what happens in the case of incremental adsorption volumetry using an intermediate dosing device (ref. 11 , 12), both volumetric techniques refered to in this paper lead to *a void volume correction which is -just as for the buoyancy correction in gravimetry- proportional to the equilibrium pressure and independent* of *the number of previous experimental points.*

Quasi-equilibrium pressure. The accuracy is of course independent of the gravimetric or volumetric method and is comparable for both equipment ,

Sample mass. Any microbalance has a maximum load (not more than 6g sample in our case) whereas there is no such limitation for quasi-static volumetry, which may then be used to study the surface roughness of relatively heavy samples.

Sample temperature. This is known to be a critical point in adsorption gravimetry. We saw in special blank experiments that with our assembly it was only when the nitrogen pressure was over 50 mtorr that the temperature difference between the sample and the liquid nitrogen bath was smaller than 0.2 K (ref. 13). Another way to check this temperature difference during an actual adsorption experiment is presented in Fig. 2 showing part of the adsorption isotherm for the nitrogen/graphite system. Here, the quasi-equilibrium pressure corresponding to the onset of the transition sub-step is taken as a sensitive thermometer. Indeed, applying the Clausius-Clapeyron equation with an adsorption isosteric heat of 11 kJ mol^{-1} (ref. 14) leads to a temperature sensitivity of 1,2 torr K^{-1}. From Fig. 2 one derives a transition pressure of 5,6 torrs, equal to that obtained by quasi-equilibrium adsorption volumetry (ref. 14). *Hence, in the BET* *region, the temperature difference is therefore smaller than 0.1 K.*

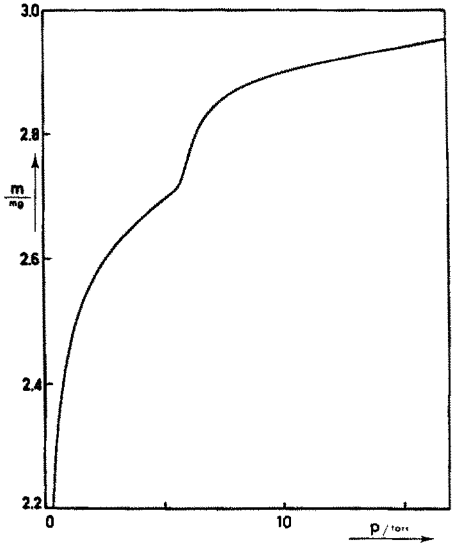

Fig. 2. Adsorption isotherm of nitrogen on graphite (10 m^2g^{-1}) at 77 K (gravimetric recording).

Pore size distribution

Here, the critical points to look at are :

The outgassing conditions. They are hardly the same in the microbalance (where the residual pressure is usually in the 10^{-3} - 10^{-4} torr range during outgassing) and in an adsorption bulb with capillary tubing (where the pressure *during* outgassing is at least two orders of magnitude higher than in the microbalance). This is why we found it necessary, especially for porous samples, to monitor and to control the outgassing in both techniques by the same basic thermal method (C.R.T.A.) so as to achieve, in both cases, the same extent of outgassing.

The sample mass. The total mass uptake during adsorption must stay within the automatic compensation range of the microbalance (here, ± 20 mg, *i.e.* a maximum of 40 mg full scale). This means for instance that the isotherm of Fig. 4 (where the uptake is *c.a.* 700 mg g^{-1}) must be carried out on a sample of 40-50 mg (or even less if one does not know the sample behaviour and therefore needs a safeguard). A sampling problem may then arise, especially for technological adsorbents.

The upper part of the isotherm. This is the part in which a difference may be observed between the isotherms obtained by the two techniques. Nevertheless, this is not the case for the isotherms presented in Fig. 3 and 4, where the

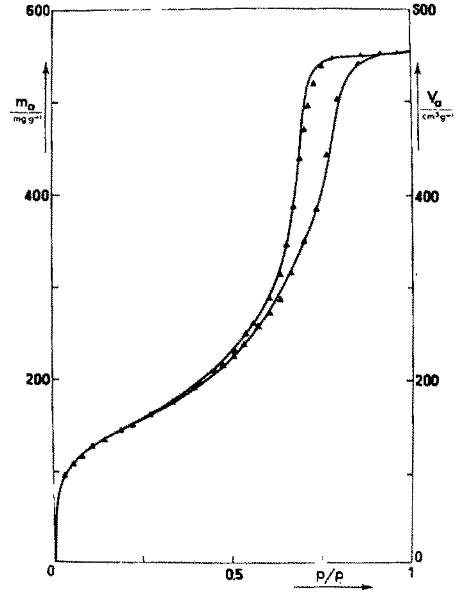

Fig. 3. Adsorption-desorption isotherm of nitrogen on a silica-gel (pore size *c.a.* 5 nm) both by gravimetry (solid line) and volumetry (points).

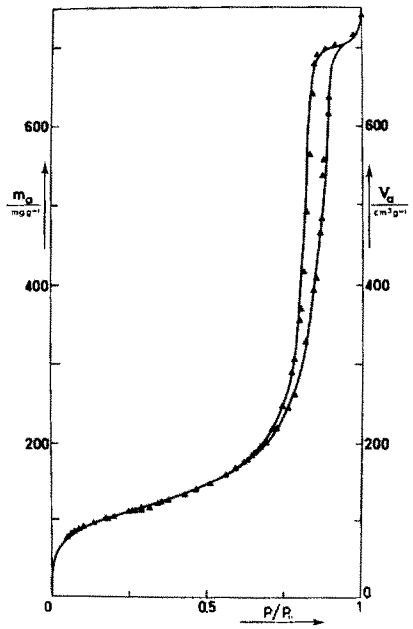

Fig. 4. Adsorption-desorption isotherm of nitrogen on a silica-gel (pore size *c.a.* 11.5 nm) both by gravimetry (solid line) and volumetry (points).

continuous line was obtained by quasi-static adsorption gravimetry and the points by conventional adsorption volumetry. Both curves show a clear upper saturation plateau. It is only when the pore size is above 25 nm that this plateau is too short to be detected by gravimetry (as we know from other experiments), the reason being the condensation which preferably takes place on the colder points of the microbalance tubings, at the level of the liquid nitrogen evaporation surface.

The extent of automaticity. Because such an adsorption-desorption isotherm is extremely time-consuming (several days), any automation like that of quasi-static adsorption gravimetry is highly appreciable.

CONCLUSION

The following conclusions may be drawn from the above comparison :

o *For specific surface areas, both quasi-static procedures* (gravimetric or volumetric) *are equivalent* (in automaticity, accuracy, resolution, time consumption) except for the smallest surface areas (*c.a.* 0.1 m^2g^{-1}) for which gravimetry is somewhat more sensitive, and for heavy solid samples for which volumetry has unlimited capacity.

o For pore-size distributions, the advantage of conventional adsorption volumetry is to detect the upper part of the isotherm, even with a pore-size larger than 25 nm, and to accept relatively large representative samples, whereas the advantage of quasi-static adsorption gravimetry is to be automatic.

o The thermal treatment and the level controlled liquid nitrogen bath can be equally good in either technique.

o *The buoyancy and void volume corrections* and their uncertainties *are the same* for the three techniques (either gravimetric or volumetric).

o We ourselves see a larger difference (in resolution, ease of use, amount of data) between quasi-static and incremental procedures, whatever the technique, than between adsorption gravimetry and adsorption volumetry.

ACKNOWLEDGEMENTS

The authors wish to thank the Bureau Communautaire de Référence for their support in the work of the Experts Groups on Particulate Reference Materials.

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