



## SOFTWARE NOTE

## COMPUTER DRIVEN APPARATUS FOR ADSORPTION MEASUREMENTS\*

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**Abstract**—The idea and programs for an automatic microcomputer driven multiple-sample apparatus for measurements of gas adsorption is presented. The Surfamat-5x system is useful for determination of specific surface area and porosity of solids by analysis of adsorption isotherms of nitrogen at the temperature of a liquid nitrogen bath.

The system consists of a five-channel measuring unit and a CP/M microcomputer-based control unit with FORTRAN/ASSEMBLER programs for control and interpretation of measurements. The measurement control/optimization and data interpretation programs were intensively developed and the MS-DOS interpretation program was prepared. Raw data stored in disk files by control programs are transferred to an MS-DOS computer for further interpretation. The interpretation program allows us to choose among many models of adsorption/desorption and condensation/evaporation in mesopores as well as adsorption in micropores depending on the kind of solid investigated.

## INTRODUCTION AND GENERAL CONSIDERATIONS

The specific surface area and porous structure are among the most important parameters characterizing solid materials being used as sorbents in separation science, environmental protection, column packings in chromatography, catalysts, etc. These two elements of "surficial properties" are strongly correlated. One should note that in extreme cases for active carbons the specific surface area may reach about 1500 m<sup>2</sup>/g. Such a highly developed area is a direct consequence of the presence of inner pores of varying size and shape. Therefore, the developments of efficient experimental techniques allowing a determination of surficial properties is of great practical importance.

Generally there are two main methods enabling determination of pore size distribution. The first is the mercury porosimetry and the second is based on the analysis of adsorption isotherms of various gases and vapours. In particular, the method based on the analysis of low-temperature adsorption-desorption data for nitrogen have become a standard method (Young & Crowell, 1962; Oscik, 1982). In order to estimate the specific surface area of a sample the adsorption isotherm is measured and then analyzed

using the well-known Brunauer-Emmett-Teller (BET) theory (Brunauer *et al.*, 1938). The BET equation of adsorption isotherm can be put into the following form:

$$y = \frac{x}{\text{Ads} \cdot (1-x)} = \frac{1}{A_m} + \frac{C-1}{A_m C} x$$

where Ads is the amount of nitrogen adsorbed at the relative pressure  $x = P/P_s$ , with  $P_s$  being the saturated vapour pressure,  $A_m$  is the so-called monolayer capacity and  $C$  is a constant. Plotting  $y$  vs  $x$  one can readily estimate both  $A_m$  and  $C$  from the linear part of the plot. Then, the value of  $A_m$  can be used to estimate the surface area from the following equation:

$$S_{\text{BET}} = A_m \sigma N_A$$

In the above  $\sigma$  is the area occupied by a single nitrogen molecule and it is usually assumed to be equal to 16.2 Å<sup>2</sup> and  $N_A$  is the Avogadro number. Of course, the BET theory suffers from well-known drawbacks (Young & Crowell, 1962; Oscik, 1982) and is based on a set of very specific assumptions that are seldom met in real systems. First, it neglects the porous structure of the adsorbing surface and treats it as a perfectly flat network of completely equivalent adsorption sites. Therefore, one also uses other theories of multilayer adsorption, such as those developed by Hüttig (Young & Crowell, 1962; Oscik, 1982), Anderson (Young & Crowell, 1962), Hasley (Young & Crowell, 1962; Oscik, 1982), Harkins and Jura (HJ), Dubinin and Radushkevich (Oscik, 1982; Dubinin *et al.*, 1947) or some modifications of the

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BET theory (Young & Crowell, 1962; Marczewski *et al.*, 1988).

Using the same adsorption-desorption data one can determine the pore size distribution, find the mean pore diameter and one can attempt to determine the shape of the pores. The physical basis of such measurements is the theory developed by Kelvin (Thomson, 1871) which provides the relationship between the pressure at which the capillary condensation takes place and the pore diameter and shape. According to the assumed pore shape one arrives to different equations, e.g. Cohan's equation (Cohan, 1938). There are many theories of capillary condensation (Barret *et al.*, 1951; Lippens & de Boer, 1965; de Boer & Broekhof, 1967a, b, 1968a-d; Derjaguin, 1940, 1967) which can be applied in the pore size distribution determination.

### APPARATUS

There are many commercially available automated units for the surface area and porosity determination. I can mention here such widely known products as Sorptomatic-1900 (Carlo Erba, Italy, Austria), Quantasorb-6 (Quantachrome Corp., U.S.A.) and ASAP-2000, ASAP-2400 (Micromeritics, U.S.A.). Such equipment is high quality but also of a relatively high price. The simplest one-channel unit costs over U.S.\$40,000. This fact and high demand for fast and reliable surface area and porosity determination results at our Faculty and industry, prompted us to construct this automated five-channel unit. It is relatively simple and cheap, whereas most stress was put on developing the software which makes it run. The construction was completed in 1991 and later developed, mainly through development of measurement concepts and strategies and creating new control and interpretive software.

The modular construction of Surfamat-5x (2 patents) is presented schematically in Fig. 1. It is typical volumetric device designed to measure static adsorption and desorption isotherms of  $N_2$  at temperatures of liquid nitrogen (about 78 K). It allows reasonable measurement of the adsorption isotherms for samples where the value (sample mass)  $\times$  (specific surface area) is greater than about  $5 \text{ m}^2$ , however, lower precision measurements (surface area determined within 10–20% error) are performed for the value over  $1 \text{ m}^2$ , however, best precision is attained when it is above  $50 \text{ m}^2$ . These limits are due to specific volumetric measurements, where the adsorption/desorption is calculated from the mass balance of the gas quantity introduced into the burette/doser volumes and measured pressures. Thus, they strongly depend on the precision of pressure transducers, volume calibration, ratio of burette volume to sample adsorption capacity, estimation of sample density and volume and system temperature stability etc.

The principle of measurements is presented below.

### MEASUREMENTS—IDEA AND STRATEGIES

The measurement objective is to measure isotherms of adsorption/desorption with approximately equally spaced data points, however some calculations require more data points (also evenly spaced). When the only information needed is BET specific surface area, then only the adsorption isotherm is measured over the range of 0–0.5 relative pressure, however for the measurements of sample porosity full adsorption/desorption measurement is required. Then for relative pressure ranges of 0–0.1 (microporosity estimation;  $t$ -plot), 0.1–0.5 (BET), 0.5–0.98 (mesopores) and close to 1.0 (total pore volume and saturation pressure) different isotherm steps are required. Control program NS5 allows us to set separate steps for

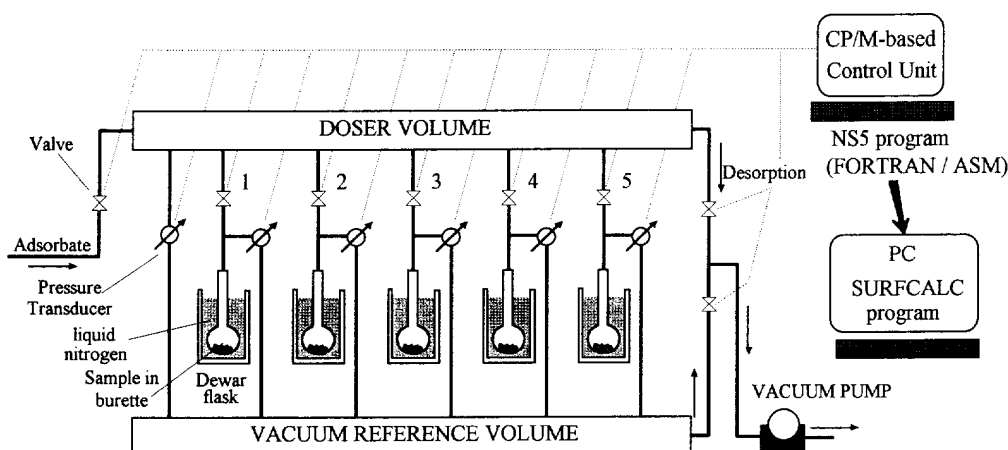


Fig. 1. Scheme of Surfamat-5x apparatus. The control unit is a CP/M based (Z80B) microcomputer. Measurement data are stored in disk files and may be interpreted by the SORPCALC program (CP/M version), or transferred to the PC for further interpretation with the new program SURFCALC (MS-DOS, version for MS-Windows, in preparation).

adsorption and desorption changing smoothly with equilibrium pressure or constant and if required, one quarter or half steps for the  $t$ -plot range and half steps for the BET range. The parameters of measurement are prepared by a separate program NDANES and stored in disk files for future reference and use for similar or the same samples.

Below, the measurement strategy (NS5 program) is roughly described:

1. Start of measurements: setting up measurement queues (active channels and channels ready for next dosing).
2. Dosing to the first channel in a queue and moving it to the end of queue: (a) for adsorption: pressure in doser is set higher than equilibrium pressure in the burette; and (b) for desorption: pressure in doser is set lower than equilibrium pressure in the burette (equally spaced points are obtained if the difference between the pressure in the doser and in the sample burette is constant).
3. If active channels queue is not empty then perform approximate measurements of pressures in all active channels; if the queue is empty then stop measurements.
4. Checking if any channel reached equilibrium (all active channels): (a) if elapsed time from dosing is too small then go to the next sample; (b) if pressure from last measurement changed to much ("slope detector") then go to the next sample; and (c) if the pressure is stable or if the maximum elapsed time from dosing is exceeded, the pressure is measured accurately; then checking is performed if and what kind of dosing is to be performed (based on: end-pressure attained, maximum number of data points exceeded, etc.). The kind of dosing is changed from adsorption to desorption (end of adsorption branch) or the next step is performed the same way—the channel is either moved to the end of the dosing queue or is set inactive, i.e. removed from queue (end of measurements).
5. If there is a channel ready for dosing: go to Step 2, if not then go to Step 3.

During measurements some intervention, i.e. changing some measurement parameters is allowed, however it is not recommended, as it may give some sharp steps on the isotherm data obtained. In some cases, however, it is reasonable—when the sample was entirely unknown and measurement parameters were set too far from the optimum values (isotherm steps very small or very big) and the current run can be a basis for setting up a more precise one.

## RESULTS

The data interpretation may be performed by using the SORPCALC program (CP/M) or after transfer-

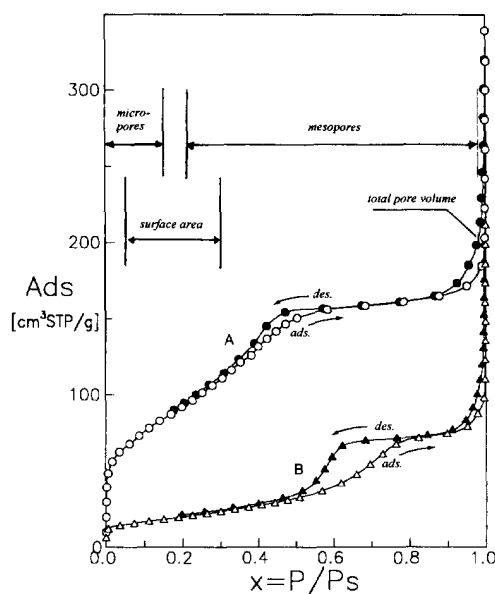


Fig. 2. Isotherms of adsorption (open symbols) and desorption (black symbols) of  $N_2$  ( $T = 78.3$  K) for monodisperse spherical  $TiO_2$  samples: amorphous (A, circles) and transformed through heating at 900 K into anatase (B, triangles). Changes in sample A induced by heating are perfectly visible and possible to estimate quantitatively. Measurements well performed with Surfamat-5x (control program NS5 and interpretation program SURFCALC). Smaller isotherm steps for  $x < 0.5$  (BET surface area region) as well as hysteresis loops and other details are visible. Ranges of data used to estimate the kind of sample property indicated are drawn schematically.

ring data files to PC microcomputer, with the new program SURFCALC. The software utilizes data in the form of a series of pressure values to calculate the adsorption and desorption branches of the isotherm and next to estimate:

- the specific BET surface area
- micropore volume using the  $t$ -plot according de Boer
- total pore volume and average "hydraulic" mesopore radius (assuming open-ended cylindrical capillaries)
- adsorption phase capacity according to the Dubinin and Radushkevich (DR) equation for microporous solids
- standard  $(\Delta v/\Delta r)$  and semi-logarithmic  $(\Delta v/\Delta \lg r)$  forms of pore-size distribution function from adsorption and desorption isotherm branches for the BJH model (Barret *et al.*, 1951), and the Dollimore and Heal model (1964) for different forms of isotherm equations for a non-porous solid
- standard  $(\Delta v/\Delta r)$  pore-size distribution from desorption data for the Dubinin condensation model (Dubinin, 1981) which utilizes the progress in the theory of capillarity made by Derjaguin (1940, 1967), Tolman (1949), Lippens and

de Boer (1965) and de Boer and Broekhof (1967a, b, 1968a, b, c, d).

In Fig. 2 the exemplary isotherm measurements, performed by using the above described apparatus and software for two samples of monodisperse spherical titania [ $\text{TiO}_2$ —for the method of preparation see Haber *et al.*, (1991)] are presented. Differences in samples caused by heating sample A (amorphous, sphere diameter 600 nm) at 900 K for 20 min to obtained sample B (anatase) are clearly visible and may be used to evaluate quantitatively the changes in sample surface area and its porous structure.

#### FUTURE DEVELOPMENT

A new construction is planned which would allow precise measurement of adsorption isotherms over the range 0.001–0.1 hPa (the current version gives good quality isotherms for pressures above 0.1 hPa) which is very important for microporous samples and also includes the possibility of using gases and vapours other than nitrogen (adsorbates such as carbon dioxide, methane, ethane and benzene at room temperature) as well as using it as the helium densitometer.

The software is being developed in order to change both control and interpretation programs to the MS-Windows platform, together with their integration into one system.

*Program availability*—Source programs (Fortran) are available upon request.

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