Automated Instrument to Measure Specific Surface Area of Powders using the Brunauer–Emmett–Teller Method

D.N.P. Ruwan Jayakantha[1,3], Nadeesha M. Gunawardana[1], S.M.M.L. Karunarathne[1], Elisabetta Comini[3], Nanda Gunawardhana[1*]
Faculty of Research, SLTC Research University, Padukka, Sri Lanka[1]
Faculty of Science, University of Peradeniya, Sri Lanka[2]
Sensor Lab, Department of Information Engineering, Brescia University, 25133 Brescia, Italy[3]

[*] nandag@sltc.ac.lk

Abstract - An automated instrument was designed to measure Specific Surface Area (SSA) of a powder material using the Brunauer–Emmett–Teller (BET) isotherm method. A material with a known SSA was introduced to make the method simpler, accurate and fast. The cost was reduced by operating the instrument at a fixed partial pressure. A piezoelectric sensor was introduced to increase the sensivity of changes in gas flow rates. The SSA analyzer is used to analyze the SSA of an unknown sample, to compare the SSA of two samples and to identify unknown samples using the SSA. The error of the instrument was found to be less than 0.1%.

Keywords: Specific surface area, Partial pressure, Piezoelectric sensor, Brunauer–Emmett–Teller (BET) isotherm method.

I. INTRODUCTION

The surface area of a material is often mutually related to rates of dissolution and other rate-related phenomena such as catalyst activity, electrostatic properties of powders, etc. Various methods were suggested in the past to measure it [1]. As the particle size decreases, surface area per unit mass increases. In powder solid materials the surface area is calculated per unit mass and called the specific surface area (SSA). In some porous materials SSA is reported high as several thousands of square meters per gram [2]. The surface area of a powder effects the intensity of interaction between two materials. SSA depends on the size of particles and surface texture [2].

In general, three types of SSA are known. First definition is the area that can be completely covered by an adsorbed monolayer of individual molecules of a reference gas adsorbate. The well-known Brunauer–Emmett–Teller method (BET method) is based on this phenomenon. The second definition is called the “geometric specific surface area” [3]. The related measurements are obtained by measuring the particle size using an optical microscopy. The third definition is the “wet surface area” [4]. This definition considers the microscopic surface texture. Wetting of particles by a liquid having a negligible angle of wetting results in creating a real phase interface between the granules and their environment. The surface area is determined on the amount of liquid needed to create an interface. The “wet surface area” is important in studies related to chemical reactions between solids and liquids. The BET method is commonly used for evaluating the surface area of powder materials [2]. However due to conditions need to be controlled and accuracy the related devices are expensive.

This work describes the design of a low cost, fully automated instrument to analyze SSA of a solid powder (SSA- analyzer). The instrument was designed using the BET principle. To make the analysis simpler and accurate a known sample was introduced.

II. THEORY

The SSA of a powder material can be determined using the following equation,

$$S = \frac{V_m}{m \times 22400} Na \qquad (1)$$

where,

S – Specific surface area ($m^2\ g^{-1}$)

Vm – Volume of gas adsorbed at constant temperature and pressure (ml)

N – Avogadro constant ($6.022 \times 10^{23}\ mol^{-1}$)

a – Effective cross sectional area of one adsorbate molecule (m^2)

m – Mass of test powder (g)

22400 – Volume (in ml) occupied by 1 mol of the adsorbate gas (Nitrogen) at standard pressure and temperature allowing for minor departures from the ideal.

By measuring the adsorbed gas volume of a SSA known sample and an unknown sample the following equation was obtained,

$$\frac{S_T}{S_R} = \frac{V_{mT}}{V_{mR}} \frac{m_R}{m_T} \qquad (2)$$

where,

S_T, S_R – SSA of test and reference samples ($g\ m^{-2}$).

m_T, m_R – Mass of powders of test and reference samples (g).

The SSA analyzer calculates the VmT/VmR ratio using equation (2) at partial pressure 0.3 and temperature -193 ^{0}C using the two signals it gets from the two sensors.

III. MATERIALS AND METHODS

A block diagram of the SSA-Analyzer is shown in Figure 01. The mass of the reference and test samples were measured using the chemical balance. Next the two sample tubes were filled with the powder samples and installed in the machine.

Then the samples were degassed in a flowing Nitrogen gas environment and were left to cool down to room temperature in the nitrogen environment. Next the partial pressure was set to 0.3 as follows, $P_{He}/(P_{He}+P_{N2}) = 0.3$ (P_{He} - Pressure of Helium, P_{N2} - Pressure of Nitrogen). After that the gas mixture was let to flow through the samples by opening valves V_1 and V_2 for about five minutes. At this point the data processing system in the software was started to collect the data. Next the valve V_2 was closed while V_1 is still open and only the reference sample was immersed in liquid Nitrogen to cool down to -193 ˚C in order to start the adsorption process. After the adsorption process is completed it is successfully identified by the software. After the adsorption was completed the V_1 was closed and V_2 was opened and the test sample was immersed in liquid N_2. Finally, the software processes the sensor signals and determined the SSA of the unknown sample.

IV. RESULTS AND DISCUSSION

To optimize the adsorption and to keep the system within the linear range of the partial pressure (0.05-0.35) the partial pressure was fixed at 0.3. According to the BET theory when partial pressure is at 0.3 the error is minimized. With the support of two valves (V_1 and V_2) gas mixture was flown through one sample at a time. As soon as the adsorption starts the out coming flow rate (detected by sensor 2) drops for some time due to the adsorption of N_2 molecules and comes back to the initial value which indicates that the sample is saturated by adsorbing nitrogen molecules. As a result of the drop in flowrate a drop in pressure occurs in the outflowing gas. This variation was detected by the pressure sensors 1 and 2. The sensor signals were analyzed and used to plot the graph of "arbitrary adsorbed gas volume" vs time. The curve increased with time when the adsorption started and came back to the initial value after a period of time, which indicated the completion of the adsorption process. Therefore, the area of the graph is proportional to the adsorbed gas volume by the sample.

When the valve V_1 closed and V_2 opened the gas flows only through the test sample. Same as the process described above with the reference sample. The software again calculates the area under the curve which is proportional to the adsorbed gas volume by the test sample. Using the data, the ratio VmT/VmR was calculated. The weights of the test and reference samples were already measured and the SSA of the reference sample was known and hence the SSA of the test sample was calculated using equation-2.

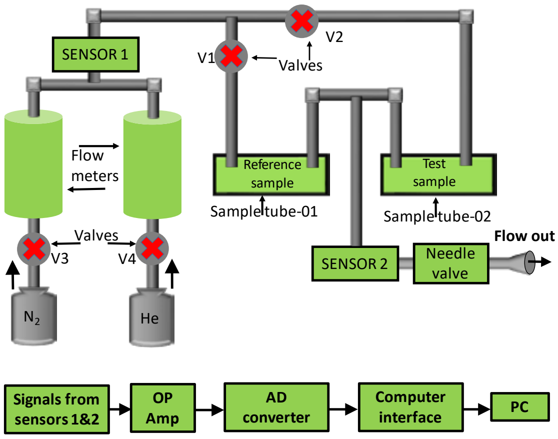

Figure 01: Basic block diagram of the SSA analyser

Four samples of activated charcoal (A, B, C, D) with different SSA values were used to calibrate the instrument and their SSA values are shown in Table 1. The measured values were highly accurate (error 0.1 %).

Table 1. SSA values of known samples.

Reference	Given Specific surface area (m^2/g)
A	1743.0
B	1663.0
C	1734.0
D	1527.0

V. CONCLUSION

Designed analyzer is capable to find the SSA of an unknown sample, to compare the SSA of two samples and identify unknown samples using the SSA. The introduction of a SSA known sample simplifies the method and reduces the cost. The error of the instrument was found to be less than 0.1%.

References

[1] Pennell, K. D. Specific Surface Area, in Reference Module in Earth Systems and Environmental Sciences; Elsevier: Amsterdam, 2016.

[2] Carman, P. C. Capillary rise and capillary movement of moisture in fine sands. Soil science. 1941, 52(1), 1-14.

[3] Farin, D.; Avnir, D. Reactive fractal surfaces. Journal of Physical Chemistry. 1987, 91(22), 5517-5521.

[4] Hwang, N.; Barron, A. R. BET surface area analysis of nanoparticles; The Connexions project, Rice University: Houston, 2011, 1-11.