Surface Measurement Systems
World Leader in Sorption Science

iGC SEA Application Note 225

Isotherm Measurements for BET Surface Area Calculations using Inverse Gas Chromatography

Majid Naderi, Jiyi Khoo, Manaswini Acharya and Dan Burnett | Surface Measurement Systems Ltd

The second generation iGC Surface Energy Analyser (SEA) has been used to measure isotherms on glass beads as well as alumina standard BET reference materials quickly and reproducibly. This study demonstrates that IGC SEA may be used to measure BET surface areas accurately at ambient temperature.

Introduction

The interaction of a solid with its surroundings is through the available surface area for adsorption of gas or vapour molecules. This also allows probing of materials surface including irregularities and pores. One of the most successful methods is based on the BET method for gas adsorption onto a solid surface. The adsorption method of Brunauer, Emmett and Teller (BET) is based on the physical adsorption of a vapour or gas onto the surface of a solid. Traditionally, sorption studies were carried out at low temperatures [1,2] to obtain nitrogen isotherms at 77 K, which were then used to calculate BET surface areas [3,4].
Considering that material behaviour varies with temperature, measurements at ambient temperatures may be more relevant and also allow the use of various gases and vapours. Inverse Gas Chromatography (IGC) has been demonstrated in various papers as a quick method to determine isotherms at finite concentration and ambient temperatures, using organic probe molecules [5,6]. This work demonstrates the capability of the second generation iGC Surface Energy Analyser (SEA) to measure isotherms quickly and reproducibly. A unique injection mechanism and variable injection pulse sizes provide major improvement in allowing the BET region of the isotherm to be obtained more accurately, especially in the case of materials with small surface areas.

Method

The specific surface areas of two nonporous alumina Reference BET Standards CRM 170 and CRM 171 (Commission of the European Communities Community Bureau of Reference Material Alumina No 170 and 171) as well as hydrophobic glass beads (Supelco) were determined by measuring the octane adsorption isotherms at 30 ^{o}C and 0% RH. Alumina CRM170 and CRM171 are standard BET reference materials with surface areas of 1.05 m2/g and 2.95 m2/g, respectively. The mean particle sizes of 9-13 µm for glass beads and ~7 µm for alumina were obtained by laser diffraction. The BET specific surface areas of the samples were subsequently calculated from the corresponding octane isotherms, within the partial pressure range of 5% to 35% P/P0.

For the isotherm determination, pre-silanised glass columns with 30 cm length and a 4 mm ID were filled with1 g of glass beads, 500 mg of CRM170 and 200 mg of CRM171 by gentle tapping. Each column was pre-conditioned for 2

hours at 30°C and 0% RH with helium carrier gas to remove any physisorbed water. All experiments were carried out at 30°C with 10sccm total flow rate of helium. All IGC SEA analyses were carried out using iGC Surface Energy Analyzer and the data were analysed using both standard and advanced SEA Analysis Software.

Results

Octane adsorption isotherms and the corresponding BET analysis plots are presented in Figure 1- 6. Table 1 summarises the BET specific surface areas of the samples obtained by IGC SEA and their reference surface area values. For the glass bead sample, the reference surface area was calculated by assuming spheres with an average diameter of 11 μm. For the CRM 170 and 171 samples, surface areas were determined using nitrogen sorption techniques at 77 K [7].

Table 1. The BET specific surface areas of the samples obtained by IGC SEA and their reference surface area values.

	IGC SEA Surface Area (m^2/g)	Reference Surface Area Values (m^2/g)
Glass beads	0.55	0.50
Reference CRM 170	1.01	1.05 ± 0.05
Reference CRM 171	2.95	2.95 ± 0.13

Figure 1 shows isotherm data for the adsorption of octane on glass beads as a function of P/P0 or concentration. The low uptake (<0.1%) and strong Type II character indicate a surface-only sorption mechanism, which allows the BET model to be appropriately applied.

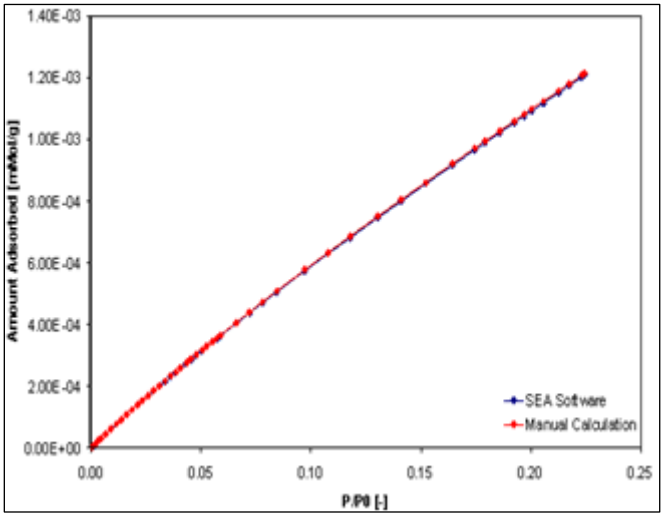


Figure 1. Sorption isotherm plot of octane on 9-13 μm glass beads at 30 °C.

The BET surface area calculations gave a good straight line data fit, shown in Figure 2, over the partial pressure range of 5% to 30%. The surface areas for the glass bead was found to be 0.5498 m2/g , which is in good agreement with the calculated reference surface area value of 0.50 m2/g, assuming 11 μm spheres.

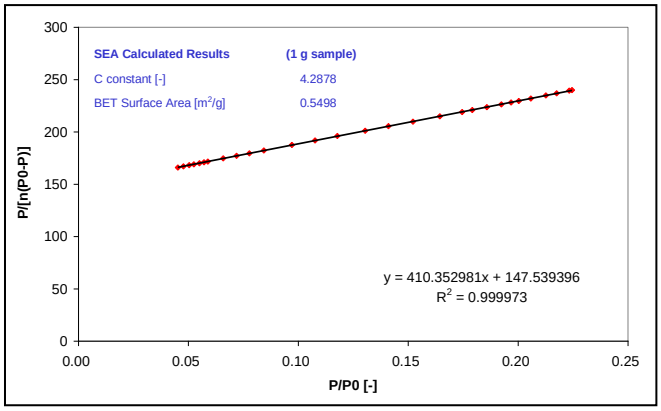


Figure 2. BET analysis for 9-13 μm glass beads at 30 °C.

Figures 3 and 4 show isotherm data for the adsorption of octane on the standard CRM 170 and CRM 171 reference materials, respectively. The isotherms show a significant uptake at low partial pressures followed by relatively smaller adsorption at intermediate vapour concentrations, which is typical type II/IV isotherm.

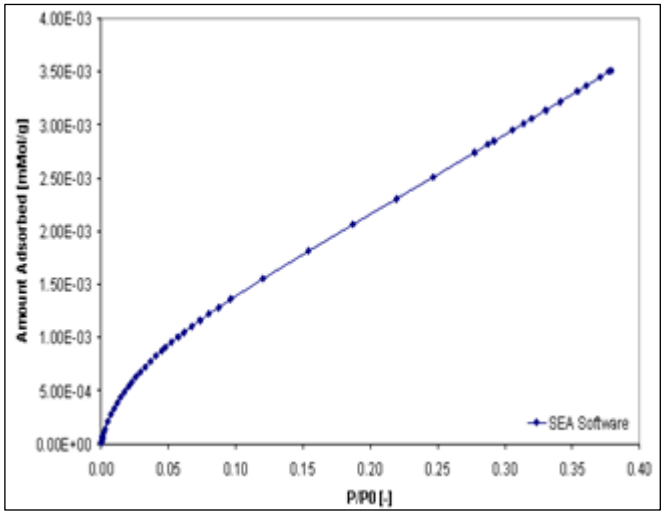


Figure 3. *Sorption isotherm plot of octane on CRM 170 at 30 ℃.*

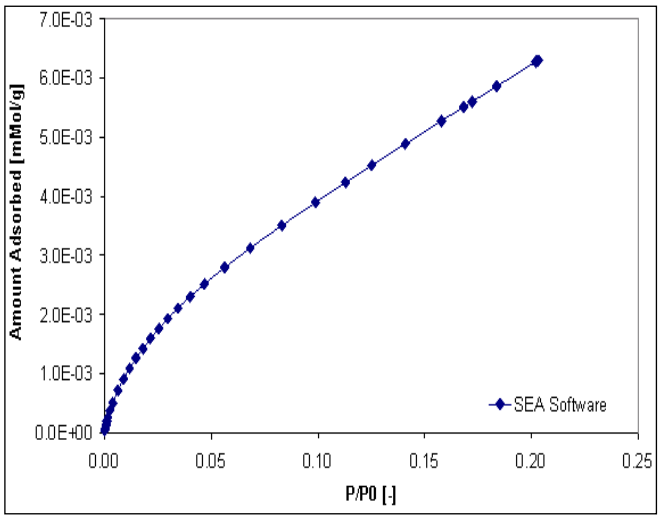


Figure 4. *Sorption isotherm plot of octane on CRM 171 at 30 ℃.*

The BET linearised plots over the partial pressure range 5% to 35% for the standard CRM 170 and CRM 171 reference materials are shown in Figures 5 and 6, respectively. The corresponding surface area values for the standard CRM 170 and CRM 171 reference materials were found to be 1.0125 and 2.9524 m^2/g , which are in good agreement with the published nitrogen surface area values of 1.05 and 2.95 m^2/g, respectively.

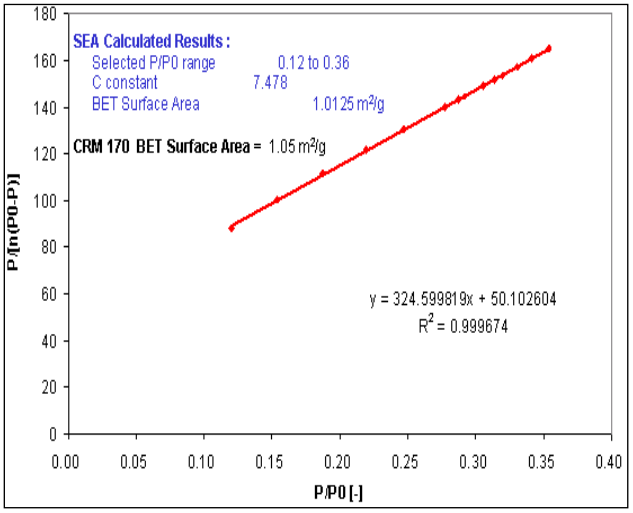


Figure 5. BET analysis for CRM 170 at 30 ℃

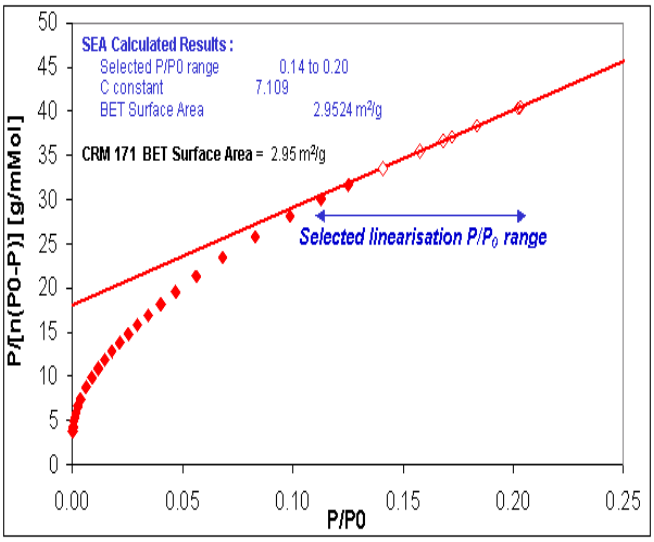


Figure 6. BET analysis for CRM 171 at 30 ℃.

Conclusion

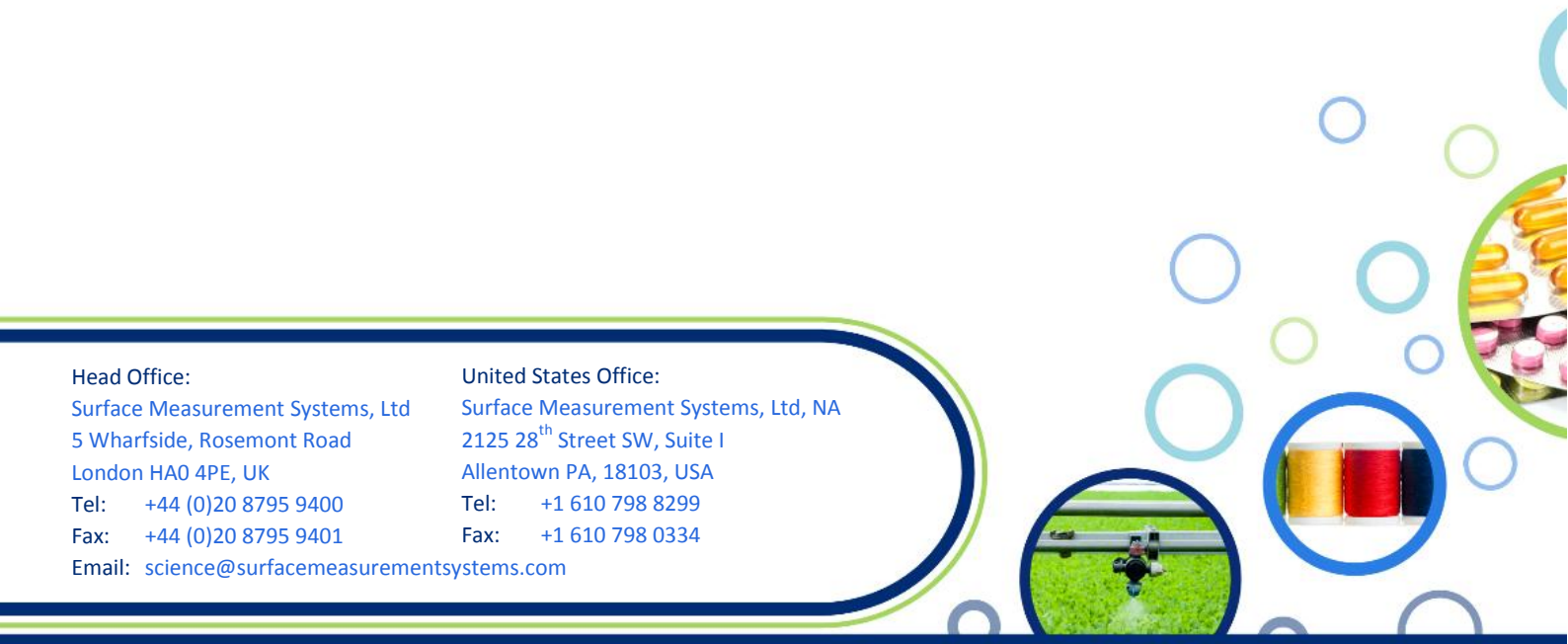
IGC SEA has shown to be an accurate technique for the determination of isotherms and derived parameters such as BET surface areas for alumina standards, allowing low surface areas to be measured. Results were in good agreement with nitrogen sorption experiments demonstrating excellent reproducibility of the data as well as the possibility of studying small sample sizes at ambient temperature and pressure with a wide range of adsorbing vapour species.

Acknowledgement:

The authors gratefully acknowledge Surface Measurement Systems former colleagues for their contributions to this work.

References

[1]Brunauer, S., Emmett, P. and Teller, E., J. Amer. Chem. Soc. 60 (1938), 309
[2]Gregg, S. and Sing, K. S. W., in "Adsorption, Surface Area and Porosity", Academic Press, New York, 1982
[3]Baumgarten, E. and Weinstrauch, J. Chromatography 138 (1977), 347
[4]Roginskii, S. et al, Dokl. Phys. Chem. 133 (1960), 717
[5Kiselev, A.V. and Yashin Y.I., Gas Adsorption Chromatography, Plenum, New York (1969).
[6]Condor, J.R and Young, C.L.. *Physicochemical Measurement by Gas Chromatography,* John Wiley and Sons, Chichester (1979)
[7]Wilson, R., Havard, D.C., Gould, D., Commission of the European Communities Community Bureau of Reference Materials , EUR 12025 (1989)



Head Office:
Surface Measurement Systems, Ltd
5 Wharfside, Rosemont Road
London HA0 4PE, UK
Tel: +44 (0)20 8795 9400
Fax: +44 (0)20 8795 9401
Email: science@surfacemeasurementsystems.com

United States Office:
Surface Measurement Systems, Ltd, NA
2125 28th Street SW, Suite I
Allentown PA, 18103, USA
Tel: +1 610 798 8299
Fax: +1 610 798 0334