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iGC SEA Application Note 208

The Measurement of Isotherms by Pulse Inverse Gas Chromatography

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Isotherm measurements provide the means to calculate BET surface areas and pore size distribution functions. Standard measurements at 77 K are restricted to very few probe molecules. Moreover, these temperatures cause long measurement times despite that they are less relevant in practical terms. Inverse Gas Chromatography provides a fast and accurate isotherm measurement in a wide temperature range and with various probe molecules. This is demonstrated in this paper by hexane and cyclohexane sorption measurements on different oxides.

Introduction

In the past, sorption studies were carried out regularly at low temperatures [1,2] to obtain nitrogen isotherms at 77 K. These isotherms were used to calculate BET surface areas and pore size distribution functions.

For practical purposes an investigation at ambient temperatures or above is of greater interest since elevated temperatures are more relevant in industrial processes and quite often, material behaviour varies with temperature. Testing at ambient temperatures also permits the use of various gases and vapours for the measurement, whereas experiments at 77 K are restricted to just a few probe molecules.

A convenient method for the study of sorption under the desired conditions is Inverse Gas Chromatography (IGC SEA). IGC SEA was demonstrated in various papers as a quick method to determine isotherms at finite concentration using organic probe molecules at ambient temperatures. From these isotherms BET surface areas and pore size distribution functions can be derived [3,4]. Due to its sensitivity IGC SEA proves especially beneficial in the determination of small surface areas.

This paper demonstrates the capability of IGC SEA to measure isotherms quickly and reproducibly. It also discusses problems and solutions related to the experiment.

Theory

Generally IGC SEA measurements can be configured in two ways: as an elution or a frontal experiment. In a frontal experiment the probe molecule is added continuously to the carrier gas, whereas a pulse measurement involves a single injection of a certain amount of vapour. The vapour is transported by the carrier gas through the IGC SEA to the column. The amount adsorbed from the sample in the column is eluted by the carrier gas and in the ideal case an equilibrium state is reached. In the case of a frontal experiment a breakthrough curve is observed. A pulse experiment results in a peak, the shape of which depends strongly on the shape of the solid-vapour sorption isotherm (Figure 1).

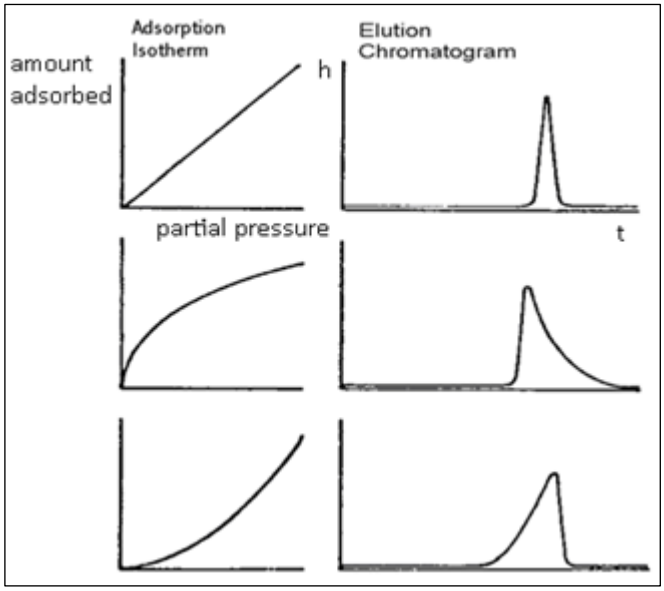

Figure 1. Correlation of peak form and sorption isotherm for finite and infinite dilution.

In the case of infinite dilution a symmetrical (Gaussian) peak is observed representing a linear (Henry) isotherm. At high concentration (finite dilution) tailing or leading will occur. In the case of a type I, II or IV isotherm there is a tailing because adsorbent/adsorbate interactions are much stronger than adsorbate/adsorbate interactions. This is usually the case when non-polar probe molecules adsorb on solid surfaces. Thus, sorption isotherms in this paper were calculated based on the method of Cremer and Huber [5].

In this calculation partial pressures are obtained from the peak height h and the net retention volume V_N from the retention time.

$$VN = j \bullet w / m \bullet (tc - t0) \bullet Tc/273 \qquad (1).$$

In Equation 1 w is the carrier gas flow rate, m the sample mass, T_C the column temperature, t_c the gross retention time, t_0 the dead time and j the James-Martin correction for the pressure drop across the column. The net retention volume is divided by the gas constant and the column temperature to obtain the pressure related retention volume.

The partial pressure is obtained from the peak height by Equation 2.

$$p = h / E \qquad (2),$$

where E is the conversion factor calculated according to Equation 3.

$$E = F \bullet w \bullet T_{loop} / (V_{loop} \bullet p_{sat} \bullet p/po \bullet 273) \qquad (3).$$

In Equation 3 F is the area under the peak, p_{sat} the saturation pressure of the gas probe molecule and V_{loop} the volume of the gas probe loop.

A plot of the pressure related retention volume versus the partial pressure represents the first derivation of the isotherm (with the pulse method only desorption data is available for these types of isotherms). The retention volumes and partial pressures can either be obtained from the maxima of peaks at different concentrations (Peak Maximum method) or from the tailing of a high concentration peak (Elution by a Characteristic Point, ECP method). Graphical or numerical integration gives the desorption isotherm in both cases.

Method

Various columns were packed with M745 supplied by Condea and zirconia VP supplied by Degussa, Germany. All sorption experiments were carried out on an SMS-*iGC* 2000. Measurements were performed with hexane and cyclohexane, supplied by Aldrich, at a He flow rate of 10 ml/min. The sample was pre-treated for 2 h at 403 K to remove impurities adsorbed on the surface.

Following this, pulses were injected by a 0.25 ml gas loop at 303 K. In the ECP experiment the adsorption concentration was chosen to be 0.95 p/po. For a peak maximum experiment measurements were undertaken at 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 0.95 p/po. Calculations were performed using the iGC Standard and Advanced Analysis Software .

Results

Figure 2 shows a series of pulses for a multiple injection experiment (variable concentration) on M745 with hexane at 303 K.

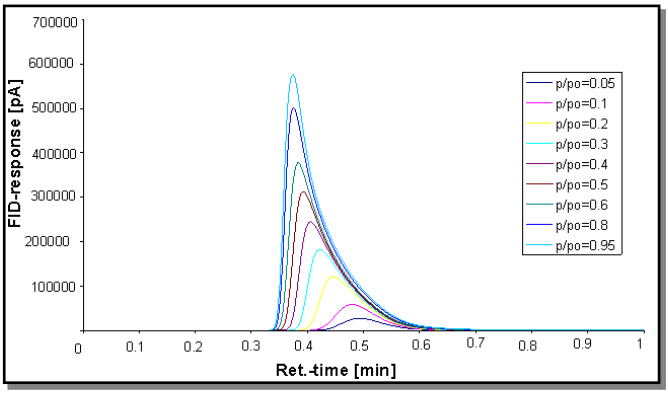

Figure 2. Pulses of different concentration of hexane on M745 at 30°C.

Ideally each peak maximum should match the tailing of the highest peak. As can be seen this is not quite the case. The deviation from this ideal behaviour is caused by gas phase diffusion effects [6]. Only in very few cases are diffusion problems addressed in the literature. The SMS Analysis Software uses a simple approach to correct for these effects. Provided the gas phase diffusion causes a broadening of the peak in the same extend in the front as in the rear, a subtraction of the front can be performed to isolate the pure desorption contribution of the rear tailing. Figure 3 demonstrates the impact of such correction.

As expected there is a remarkable influence of the gas phase diffusion, which can be recognised by comparing the isotherms for the Peak Maximum and uncorrected ECP. The diffusion correction has a significant impact on the isotherm although it still doesn't give a match with the Peak Maximum isotherm. The difference between Peak Maximum and diffusion corrected ECP is smaller for lower uptake but increases with increasing uptake and material surface area.

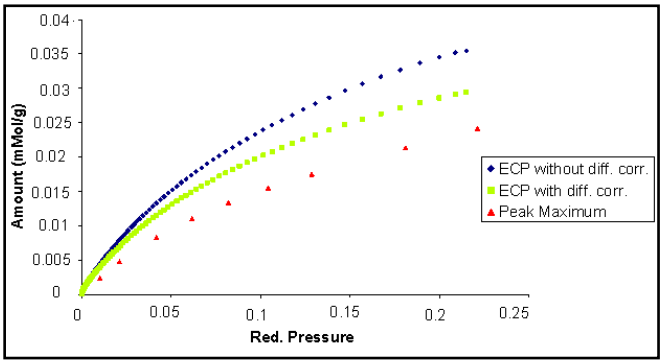

Figure 3. Impact of a diffusion correction for hexane isotherms on M745. (◊) ECP isotherm, (□) diffusion corrected ECP isotherm and (Δ) Peak Maximum isotherm.

Another effect, which might have to be taken into account at finite dilution conditions, is the concentration perturbation. The IGC SEA theory assumes ideal, laminar flow, which is not affected by the injection of the probe molecule. At infinite dilution this is certainly a valid approximation as small amounts have a negligible influence upon the carrier gas flow rate. However, at finite dilution this effect can become significant. Conder and Young suggested a mathematical correction for this perturbation [7]. The impact of this correction is investigated in Figure 4 for the maximum adsorption concentration used in this study. As the figure demonstrates, the influence of the concentration is rather small compared to the significant differences between corrected and non-diffusion corrected ECP isotherms. Thus, this effect is negligible in the considered case. However, this is not necessarily true for every system. Therefore, it is recommended to investigate the impact of concentration perturbation for any new adsorbate/adsorbent system.

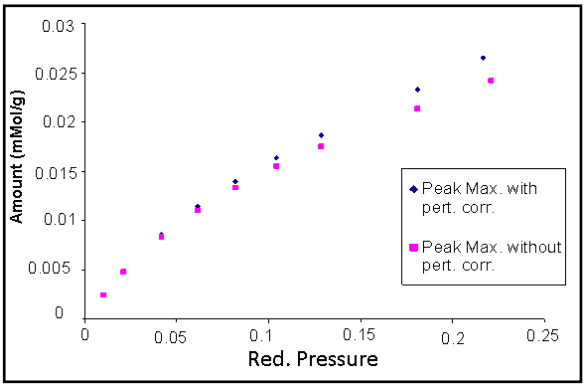

Figure 4. Peak maximum sorption isotherms for hexane on M745 with and without perturbation correction.

In order to check reproducibility, experiments were undertaken with different columns. Columns were packed with different amounts of material to investigate the influence of packing on the results. The resulting isotherms are shown in Figure 5.

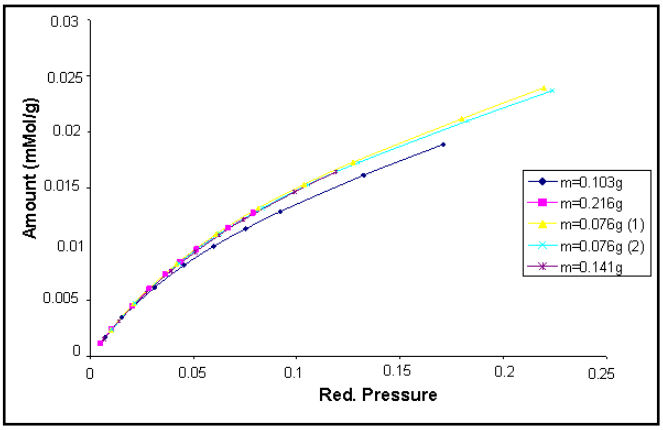

Figure 5. Sorption isotherms for hexane on M745 measured on different columns.

The reproducibility for both column-to-column and experiment-to-experiment is very good and demonstrates that often-expressed concerns about packing issues in IGC SEA measurements are unfounded. Although the amount of material doesn't show any significant influence on the results, it is nevertheless recommended to use a column-packing device to provide a reproducible packing procedure.

Peak Maximum (PM) and diffusion corrected ECP isotherms have been used to calculate surface areas according to BET [1]. The surface areas for both investigated oxides are well known from nitrogen adsorption measurements. Table 1 summarises results obtained by IGC SEA and static-volumetric measurements. Values marked with a star (*) are manufacturer data, all other static-volumetric measured values were taken from [8].

Table 1. BET surface areas in [m^2/g] from IGC SEA and static-vol. measurements with diff. probe molecules

Probe molecule	Technique	a_m (A^2)	M745	Zirconia VP
Hexane (303 K)	IGC, PM	51.5	7.59	-
Hexane (303 K)	IGC, ECP	51.5	8.81	42.86
Cyclohexane(303 K)	IGC, ECP	39.0	8.40	-
Nitrogen (77 K)	Stat.-vol.	16.2	8.07	~43*
Argon (87 K)	Stat.-vol.	14.3	7.66	-
n-Butane (273 K)	Stat.-vol.	32.2	9.50	-
C4F8 (273 K)	Stat.-vol.	36.3	7.15	-
CO_2 (273 K)	Stat.-vol.	18.1	7.26	-

The M745 is an α-alumina, which is used as a certified reference material. The reference material has a surface area of 9.6 m^2/g (measured by nitrogen at 77 K).

The IGC SEA results are well within the error margin of the surface area determination with different probe molecules. These variations are usually caused by the cross sectional area (a_m), which can be only estimated for the BET calculation. This is due to the variable geometry on different surfaces. The assumed values for the cross sectional area are included in Table 1.

A comparison of Peak Maximum and ECP values shows that corrected ECP results are constantly higher, which was expected from the higher y-values on the isotherm. However, the differences

are rather small compared to the uncertainties introduced by the cross sectional area.

Therefore, the ECP method can be used to measure BET values in this case with a reasonable accuracy and an unattainable speed due to the fact that only one high concentration injection is required. The measurement (without pre-treatment) took not more than 15 min and required not more than 70 mg of material.

Conclusion

IGC SEA was demonstrated to be a fast and accurate technique for the determination of isotherms and derived parameters such as BET surface areas for oxides. Results were in good agreement with static experiments, which proofed contact times to be sufficient for equilibrium. The reproducibility was shown to be excellent. Differences in results for the ECP and the Peak Maximum method due to gas phase diffusion effects could be reduced by introducing a simple diffusion correction. Thus, the ECP method can be used as an extremely fast tool for BET measurements for smaller surface area materials. For higher surface area materials differences between Peak Maximum and ECP method might become more significant.

Acknowledgement:

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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
[5]Cremer, E. and Huber, H., Gas Chromatography, Intern. Symp. 3 (1962), 169
[6]Thielmann, F. and Butler, D., Application Note 201, SMS UK, London 1999
[7]Conder, J.R. and Young, C.L., Physicochemical Measurement by Gas Chromatography, John Wiley and Sons, Chichester, 1979
[8]Florian, I., PhD Thesis, Berlin 1999

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