

Review

Introduction into the characterisation of porous materials by inverse gas chromatography

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Abstract

Modern methods for the characterisation of porous materials are probably as numerous and diverse as applications of porous solids. In recent years interest has grown in a deeper understanding of surface phenomena beyond the usual description of surface area and adsorption isotherm. This has led to an introduction of more sophisticated approaches, which allow for a study of thermodynamic and kinetic information. One technique, which has been shown to be very valuable is inverse gas chromatography (IGC). Due to its increasing application in industry it is the intention of this short review to introduce the principals as well as the more common applications of IGC. The methods and parameters to be discussed include isotherm determination, the measurement of surface and free energy as well as the calculation of acid–base parameters. Further, the determination of the surface heterogeneity and heat of sorption is shown. The measurement and calculation of diffusion parameters is also briefly described. It is also the intention of this paper to discuss experimental aspects and common misconceptions.

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Keywords: Reviews; Inverse gas chromatography; Porous materials; Dynamic sorption; Adsorption

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1. Introduction

Inverse chromatography can be considered as a dynamic sorption technique. Unlike in analytical chromatography the stationary phase is the sample under investigation while a substance in the mobile phase acts as a probe molecule. This

means the roles of the phases are inverted and this is where the name inverse chromatography comes from. An empty column is filled with the (porous) material under investigation (adsorbent) and the probe molecule (adsorbate) in the mobile phase probes the surface of the adsorbent.

Inverse chromatography can be utilised in the gas phase as well as in the liquid phase. Although there is a significant interest in the field of inverse liquid chromatography (ILC) only little work was done so far compared to the numerous publications on inverse gas chromatography (IGC) found in literature.

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It is for this reason that this paper will entirely focus on IGC. Readers interested in ILC applications in the field of porous materials can find a good introduction in refs. [1,2].

IGC is usually used as gas–solid chromatography (in older literature often referred to as GSC), meaning the probe is a gas or a vapour interacting with the solid sample. A less frequently-used but also interesting variation of IGC is gas–liquid chromatography (in older literature often referred to as GLC) where the probe is again a gas or a vapour but the stationary phase is a liquid. Of course only liquids with a considerable viscosity, which have been “coated” on an inert carrier material can be investigated [3].

Subsequent sections will give examples of important applications and actual advances.

2. Experimental

IGC was developed in the 1950s. Early work was done in the characterisation of catalyst support materials such as alumina, silica or activated carbon [4].

IGC measurements can be carried out using a pulse or frontal technique. In a pulse experiment a certain amount of the probe molecule is injected. This pulse is transported by the mobile phase (carrier gas) through the system to the column with the solid sample. Subsequently, adsorption and desorption occurs and the result is a peak in the chromatogram. An alternative is the frontal technique. In this case the probe molecule is added continuously to the carrier gas and the chromatogram shows a breakthrough curve [3]. The benefit of the frontal technique is that equilibrium can be always established due to its continuous nature while pulse chromatography requires the assumption of a fast equilibration of the probe molecule adsorbing on the surface.

Whether or not a pulse experiment represents (quasi-)equilibrium values depends strongly on the carrier gas flow rate. Generally it can be said that the lower the flow rate the more likely a system is in equilibrium [13]. On the other hand low flow rates mean longer experimental times and broader peaks. The latter might reduce the accuracy of the retention time determination. For this reason it is advisable to repeat the experiment at different flow rates and determine the optimum via the Van Deemter equation [39]. The situation becomes more complex when an adsorbent exhibits more than one kinetic regime, e.g. due to different types of porosity. In this case experiments could be conducted under different conditions in order to investigate them individually.

A variation of a classical frontal experiment is the continuous flow method as described first by Nelsen and Eggersten [5]. In this approach the column can be separated from the vapour generation when the concentration is altered and then reconnected after the flow has been stabilised. Depending on whether the new concentration is higher or lower adsorption or desorption will occur, which is detected as a negative or positive “peak”, respectively. The area under each peak is directly related the amount adsorbed/desorbed. This

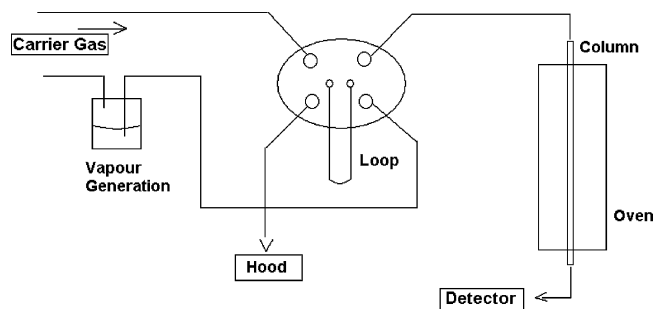


Fig. 1. Schematic diagram of an IGC experimental set-up for pulse chromatography with headspace injection via a probe vapour loop.

approach is used in several commercial instruments designed for a fast (dynamic) determination of BET surface areas. It is important to highlight that this method cannot be considered as inverse chromatography since the experiment is independent of the retention time. For this reason the method should not be discussed as IGC approach.

Classical frontal analysis on the contrary measures the retention behaviour and, is therefore, an IGC method. However, a majority of all publications is describing pulse experiments since they are faster, easier to control and more accurate, especially if interactions between probe and solid are rather weak. If, on the other hand “slow” equilibria are the subject of investigation the frontal method can be considered as a useful alternative.

Fig. 1 shows a simple schematic of an IGC experimental set-up for pulse chromatography using a vapour headspace injection system. In this case a carrier gas is passed through a reservoir containing the probe molecule in its liquid form. This way the carrier gas is saturated with the probe molecule and then flowing through the injection loop. Concentration and amount of probe molecule can be controlled via the temperature in the reservoir and the loop volume. This “saturated” carrier gas stream is then injected into another, pure carrier gas stream.

Alternatively the “saturated” carrier gas can be pre-diluted by an additional flow of carrier gas prior injection. In some publications injections have been carried out with a syringe via the manual injector port of the chromatographic device. In that case injections can either consist out of vapour/gas or the liquid directly. However, a headspace loop injection system delivers potentially more reproducible injection volumes in the author’s experience. Typical carrier gases are helium or nitrogen. In older publications other gases have been used, e.g. hydrogen. However, it should be considered that some less inert gases could show significant interaction with the solid sample under experimental conditions. It is also important to insure a sufficient purity and dryness of the gas source since some adsorption processes are highly sensitive to traces of impurities, in particular moisture.

After the injection of the probe molecule adsorption takes place at the sample in the column followed by desorption. These interactions cause retention, similar to analytical

chromatography. For this reason the primary information of an IGC experiment is the retention time, or to be more accurate the gross retention time. Additionally the dead-time of the system has to be determined. The dead-time is the time the probe molecule would require to travel through the system without any interaction. Since this cannot be measured directly the dead-time is usually determined with another probe molecule of similar structure but negligible interaction (sometimes called “tracer”) under experimental conditions or at least with interactions weak enough to ensure a fast elution by the carrier gas. A popular molecule for the dead-time measurement is methane but, depending on the detector and the adsorbent system also argon, nitrogen or hydrogen may be used. There have also been suggestions for mathematical corrections in the literature [40,41].

The retention time is measured by typical chromatographic detection methods such as flame ionisation (FID) or thermal conductivity (TCD) detector. The FID has the benefit of a higher sensitivity but is limited to mainly organics while the TCD is more versatile but very limited in sensitivity [39]. Occasionally mass spectrometric detectors are also used. This is particularly interesting for experiments where two or more probe molecules are injected simultaneously (competitive adsorption).

As far as the columns are concerned they are either glass or metal tubes. For some polymer studies coated capillary columns have been used in the literature [6] but it is obvious that this is no appropriate way to investigate porous adsorbents on a routine basis. The literature describes a vast amount of different column length and diameters for different applications. However, there are some criteria that help to select the right column length and diameter. The diameter should be generally rather small to keep gas-phase diffusion effects to the minimum. On the other hand, it can be beneficial to have wider diameters if materials with small particle sizes have to be packed in order to avoid a big pressure drop. The column length is not as crucial as the bed length of the packed stationary phase. Usually packed beds are supported on a porous filter or hold in place with glass wool plugs. For this reason the column can be longer than the packing. However, it is advisable to keep the column length close to the typical bed length for an application to avoid additional peak broadening due to gas phase diffusion. The length of the packed bed depends entirely on the uptake capacity of the sample and the amount of vapour injected. This is particularly important in the case of pulse experiments. It must be insured that the retention is strong enough (good separation between probe and tracer peak) to obtain reproducible and accurate results. This can be cross-checked by repeating the experiments with different column masses. If the final results (the parameters measured) are mass-independent it can be concluded that enough mass has been used in the column in relation to the amount of probe molecule injected. The quality of the results depends of course significantly on the technical sophistication of the apparatus used. Simple conversions of regular gas

chromatographs usually do not deliver the required accuracy and reproducibility without mayor modifications and improvements of the experimental set-up. Critical system components include the column oven temperature stability and uniformity, the control of the carrier gas flow rate, the injection system (for reproducible injection quantities) as well vapour generation system (temperature stability and accuracy). Generally it can be concluded that the more sophisticated the technology the shorter the required column length, and therefore, the faster the experiment without any compromise in accuracy and reproducibility.

3. Methods and applications

After the determination of gross- and dead-retention time the net retention volume V_N can be calculated as shown in Eq. (1) [3]:

$$V_N = \frac{j}{m} \cdot w(t_R - t_0) \cdot \frac{T_S}{T_{Ref}} \quad (1)$$

In Eq. (1) T_S is the column temperature; $T_{Ref.}$, reference temperature for the flow rate determination; m , sample mass; w , exit flow rate at 1 atm and the reference temperature; t_R , retention time for the adsorbing probe and t_0 is the mobile phase hold-up time (dead-time). j is the James–Martin correction, which corrects the retention time for the pressure drop in the column bed.

The net retention volume is related to the surface area and surface energy. Simply speaking: the higher the surface area and energy, the higher the retention time, and therefore, the retention volume.

Before we investigate this relationship any closer the determination of the key parameters surface energy and uptake (which is related to the surface area) should be described.

3.1. Isotherm measurements

Most surface area measurements are based on the determination of an adsorption isotherm of a non-polar probe molecule. Although there is a wide variety of probe vapours and gases available [7] nitrogen adsorption at 77 K has been established as a standard. Once the adsorption isotherm has been determined the BET equation [8] can be applied:

$$\frac{p}{n(p_0 - p)} = \frac{1}{n_m c} + \frac{c - 1}{n_m c} \frac{p}{p_0} \quad (2)$$

The BET equation assumes a monolayer/multilayer formation mechanism. When the partial pressure increases there is initially adsorption predominately on the surface until the (statistical) monolayer is completed. The amount adsorbed at this point is called the monolayer capacity n_m . Other parameters in the BET equation are the amount adsorbed (or desorbed) n at partial pressure p , the saturation pressure p_0 and the constant c which is related to the heat of sorption.

If the monolayer capacity has been determined and the cross sectional area a_m of a probe molecule is known the surface area can be calculated [8] as shown in Eq. (3):

$$S_{\text{BET}} = a_m n_m N_A \quad (3)$$

where a_m and n_m have the same meaning as before and N_A is the Avogadro constant.

Most commercial instruments for the determination of the BET surface area and isotherms are either static-volumetric devices [7], dynamic gravimetric techniques [9] or continuous flow methods as described above. Nevertheless, IGC can be applied for the determination of an adsorption isotherm, too. The retention time is measured as a function of concentration (partial pressure). This can be done in two ways: either a single pulse (or breakthrough curve) is injected for each concentration and the retention time is determined from each peak maximum (or breakthrough point, respectively) or the same information is obtained from just one single injection. The latter is called elution of a characteristic point, ECP (for a pulse) or frontal analysis of a characteristic point, FACP (for a frontal experiment). These methods rely on the correlation between the elution boundary and the isotherm shape, which is illustrated in Fig. 2 for a pulse chromatogram.

The theoretical treatment of such measurements was derived in parallel by Cremer and Huber [10] and Roginskii et al. [11]. Both approaches are similar and became the most applied methods for the calculation of isotherms. In the case of a (non-specific) physisorption process type II or type IV

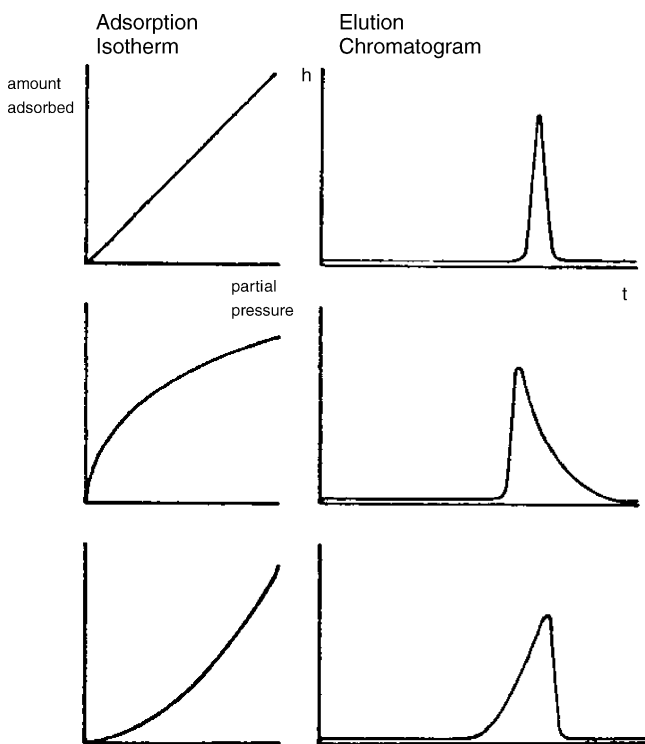


Fig. 2. Correlation of peak form and sorption isotherm for finite and infinite dilution.

isotherms are often observed [36]. This corresponds to a tailing in the chromatogram. Since pulse chromatography is more common in literature the ECP calculation is explained here [10,46]. The peak height h is directly related to the partial pressure p and can be converted as shown in Eq. (4):

$$p = \frac{hqRT_S}{Fw_S} \quad (4)$$

In Eq. (4) F is the area under the peak; q , number of moles probe injected; R , gas constant and w_S , flow rate in the column. T_S has the same meaning as above.

For a tailed peak the retention volume is the first derivation of the amount desorbed (Eq. (5)). Thus, integration provides the amount desorbed n , and therefore, the isotherm:

$$n = \frac{1}{m} \int \frac{V_N}{RT_S} dp \quad (5)$$

In Eq. (5) m , V_N , R and T_S have the same meaning as above.

In the case of a type III or type V isotherm adsorption information would be obtained [3].

Pulse IGC is a discontinuous method and the equilibrium concentration is always lower than the injection concentration. For this reason simple pulse IGC is usually limited to the low concentration range up to the monolayer coverage. However, the sensitivity and speed of IGC makes it an ideal tool in this region. The example in Fig. 3 shows the determination of a propene isotherm on a metal support catalyst at room temperature.

Another application at low concentration is the measurement of Henry isotherms and constants. In this range the uptake is independent of the surface coverage. The isotherm, is therefore, linear and the peaks in the chromatogram are (nearly) symmetrical. This region is called the infinite dilution range and interactions with the vapour phase probe molecules occur predominantly via the high-energy sites of the solid surface. This regime is ideal for the measurement of thermodynamic parameters since they can be obtained with the highest sensitivity. The span of the infinite dilution range depends on the probe molecule and the heterogeneity of the material. Especially for polar probe molecules adsorbing on very heterogeneous surfaces non-symmetrical

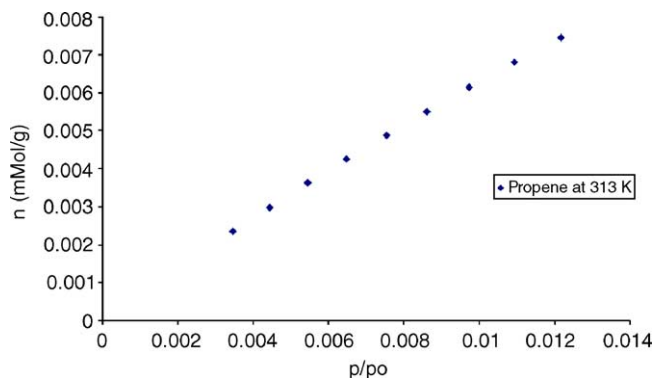


Fig. 3. Desorption isotherm of propene on a metal-support catalyst at 303 K and 10 ml/min carrier gas flow rate from a peak maximum calculation.

peaks are often observed even with the smallest injection size/concentration. This suggests that the values obtained under these conditions are not truly representing Henry conditions [42] although they are still useful for practical considerations.

3.2. Surface energy and free energy

One of the most commonly measured parameters for the description of the energetic situation on the surface of a solid is the surface energy. The surface energy is defined as the energy required to form (or increase the surface by) a unit surface under reversible conditions and is the analogue to the surface tension of a liquid. This means in practical terms that the higher the surface energy the more reactive the surface. This can affect for example catalytic activity [12] or the strength of particle–particle interaction [13].

The dispersive surface energy can be obtained from a plot of the logarithm of the retention volume of a series of alkane probe molecules (multiplied by the column temperature and the gas constant) versus the product of (square root of the) liquid tension and molecular area [14]. The result is a straight line and the dispersive surface energy γ_S^D is calculated from the slope according to Eq. (6):

$$RT \ln V_N = 2N_A(\gamma_S^D)^{1/2} a_m(\gamma_L^D)^{1/2} + C \quad (6)$$

In this equation γ_L^D is the liquid tension of the probe molecule and a_m its cross sectional area, C is a constant. The other parameters have the same meaning as above.

A somewhat similar approach is the increment system first suggested by Dorris and Gray [15]. This calculation considers the contribution of a methylene group in the alkane series to the free energy of (de)sorption. Schultz et al. [14] found similar results for both methods on carbon fibres.

In order to obtain the specific energy contribution polar probe molecules need to be injected as well. If there is a considerable specific contribution points representing a polar probe are located above the straight line. The difference is equal to the specific component of the free energy of desorption ΔG_{SP} (Eq. (7)):

$$\Delta G_{SP} = RT \ln V_N - RT \ln V_N^{\text{ref}} \quad (7)$$

Other methods use a plot of $RT \ln V$ versus the boiling point [16], the vapour pressure [47] or the polarisability [17]. The latter approach is a thermodynamically more robust method for the determination of the specific free energy and was found to be superior for the description of adsorption of weaker polar probes on highly energetic surfaces. Nevertheless, the former calculation by Schultz is more commonly applied, probably due to its simplicity.

From the specific free energy acid–base numbers can be calculated if an appropriate concept is applied.

The study of acid–base properties by IGC has the benefit that changes in the orientation of surface groups can be studied. Those changes are not necessarily related to variations in composition. For this reason spectroscopic

methods are less appropriate for the study of these effects [18].

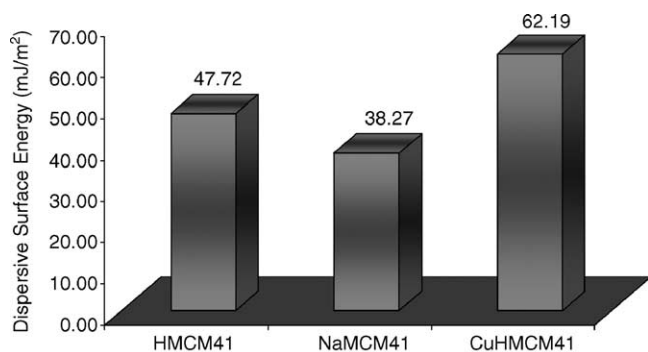
The most common approach for acid–base calculations used in IGC is the Gutmann concept [19]. Although this is very useful for semi-quantitative studies it suffers from the fact that the acid–base numbers obtained are dimensionless and can only be used for relative comparison. An alternative is the van Oss concept [20], which provides acid and base numbers in the same unit as the surface energy. Unfortunately, in its original form this equation can only be used for relative comparison due to inaccurate starting parameters leading to an overestimation of the basicity [21]. Della Volpe and Siboni [21] suggested improved input parameters to overcome this problem. However, its applicability for IGC is still under discussion [43].

Due to the high sensitivity of IGC at infinite dilution differences between materials can be detected which cannot be identified by any other technique, including wettability. This makes IGC an ideal tool for the study of batch-to-batch variation problems as they can occur due to processing and manufacturing but also for the study of surface modifications. The latter should be demonstrated by means of ion-exchanged MCM-41 materials (for details regarding the material see ref. [22]).

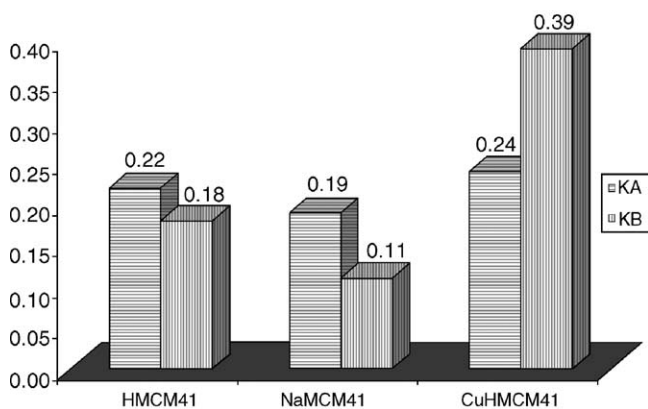
The MCM-41 mesoporous molecular sieve material has attracted attention of researchers in academia and industry because of large pore, high surface area, thermal stability and mild acidic properties. Development of proton and metal modified mesoporous molecular sieve catalysts is important in order to meet the increasing demand for processing of heavy oil fractions to value added products and to synthesise fine chemicals using heterogeneous catalysts. Cu modified MCM-41 is a potential catalyst for the synthesis of fine chemicals, hydrocarbon transformations and environmental catalysis. In order to understand the role of Cu and the changes of the MCM due to ion-exchange, surface energetics and acidic–base properties have been studied. As displayed in Fig. 4a and 4b Cu-MCM-41 catalysts show a significantly increased surface energy and acid–base interaction compared to H-MCM-41, which agrees well with an increased catalytic activity of the Cu-form as described in ref. [22]. The acid–base chemistry changes at the same time from slightly acidic or neutral for the H-MCM-41 to significantly basic for the Cu-MCM-41.

The native Na-form has the lowest energy and proton exchange causes an increase in the dispersive and specific energy. The acid–base properties suggest a significant increase in the base values while the acidic contribution increases only slightly.

Before other IGC applications are described let's return to the question of the impact of particle size (change in surface area) on the surface energy results obtained by IGC at infinite dilution. Although in many cases an increase of surface energy is observed when the surface area of a material is increased (e.g. milling) this is not an intrinsic relationship. A higher surface area means an increase in the



(a)



(b)

Fig. 4. (a) Dispersive surface energy values for ion-exchanged MCM-41 materials. Measurements were carried out at 373 K by injecting a series of alkanes from hexane to nonane. (b) Acid–base numbers according to the Gutmann concept for ion-exchanged MCM-41 materials.

number of units surface while an increase in the surface energy means a change in the concentration of active sites or even a change in their composition per unit surface.

For this reason there are many cases where an increase in surface area is observed but a decrease in energy. A good example is the comparison of the three activated carbons in Fig. 5. These three carbons originate from different starting materials and have different properties and applications.

The figure shows that the F400 material (Chemviron) has the highest dispersive surface energy, followed the ST4

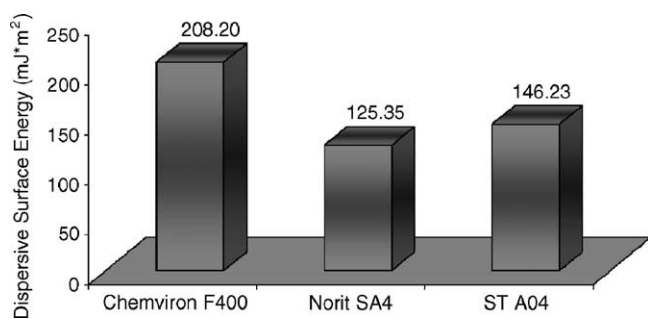


Fig. 5. Dispersive surface energies of three different types of activated carbon. Measurements were carried out at 623 K by an injection of a series of alkanes from hexane to nonane.

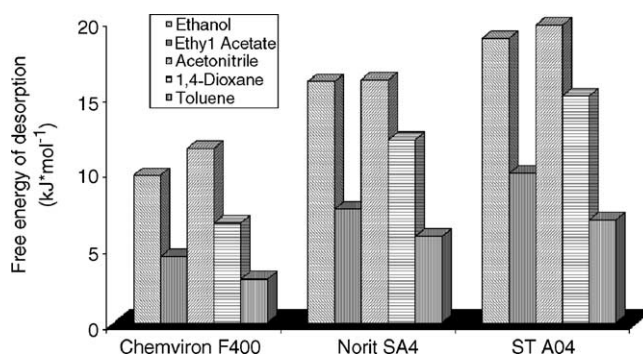


Fig. 6. Specific free energies of interaction for three different types of activated carbon, analysed according to the polarisation approach. Measurements were carried out at 623 K.

(Norit) and the STA04 (Imperial College, London) samples. Although not shown here a very similar trend was observed for the BET surface areas. However, when the specific interactions are considered a different picture is obtained as shown in Fig. 6.

Although the general trend in the surface chemistry seems to be similar for all three samples it can be clearly seen that the STA04 material now shows the strongest specific interactions, followed by the ST4 and the F400 samples. Therefore, the trend is the opposite compared to the dispersive interactions. This example also demonstrates that one must be careful in drawing conclusions regarding the adsorption of highly polar molecules based on simple BET measurements.

Similar effects have been observed in the literature, even when milled materials are compared. A good example is the work of Papirer et al. [23]. These researchers have investigated the impact of different milling procedures on an α -alumina. They found that all milling processes caused an increase in the dispersive surface energy but a decrease in the specific interaction for acidic and basic probe molecules. This was explained by amorphisation accompanied by chemical rearrangements.

3.3. Heat of sorption

Green and Pust were amongst the first to give a detailed explanation regarding the determination of the heat of (ad)sorption. They conducted measurements on alumina, silica and charcoal [24].

The principle is based on a variation of the temperature over a small range. The same probe molecule is injected at each temperature under infinite dilution conditions. The retention volume is then plotted in its logarithmic form versus the inverse temperature. The value for the heat of sorption can be obtained from the slope of the resulting straight line. This is shown in Fig. 7 for the interaction of carbon black with heptane between 385 and 397 K. The heat obtained was 64.6 kJ/mol.

A common mistake in the literature is that the temperature range chosen is too broad so that the assumption of

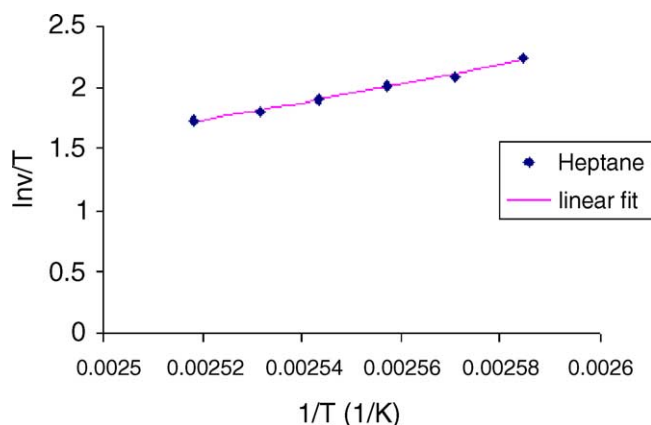


Fig. 7. Heat of sorption plot of heptane on carbon black N115. Measurements were carried out at infinite dilution in a pulse experiment between 385 and 397 K.

a constant heat of sorption is not valid. It should also be remembered that the heat of sorption depends on both the probe molecule and the surface properties. For this reason this parameter is less useful for the description of the energetic situation on the solid surface. The surface energy concept is much more appropriate for this purpose (as described above). However, the heat of sorption is a very useful parameter for the description of the interaction between certain vapour molecules and the surface. These numbers have been successfully used in catalytic and adsorbent applications where the knowledge of these interactions is essential for the understanding of the process [25].

3.4. Surface heterogeneity

Despite its huge potential IGC at infinite dilution could be criticised for the fact that only high-energy sites are considered under these conditions [48]. It is for example possible that in some cases the distribution of active sites is more relevant for the practical properties of a material than the high-energy sites. The distribution of the energy, often called surface heterogeneity is particularly important when composites are considered. These distribution functions are available by IGC when measurements are carried out at finite concentration. By increasing the concentration, an increasing number of less active sites is involved in the interaction with the probe molecule, depending on the heterogeneity. The possibility to characterise the heterogeneity profile of a surface by IGC was recognised in the 1970s. Several approaches have been published since. A good overview can be found in ref. [26].

The energy heterogeneity can be described either by the adsorption energy distribution or the adsorption potential distribution. The latter one is used here since it was found to be less affected by experimental noise and to produce more reliable results. A good description of the calculation of adsorption energy distribution functions is given in the literature [27].

The adsorption potential distribution can easily be calculated from the sorption isotherm [28]. The isotherm is derived from an IGC pulse or frontal measurement as described in an earlier section. In order to obtain the distribution function the partial pressures are converted into the adsorption potential A according to Eq. (8):

$$A = RT_S \ln \left(\frac{p_0}{p} \right) \quad (8)$$

where p is the partial pressure; p_0 , saturation pressure; R , gas constant and T_S the column temperature.

The distribution parameter Φ represents the first derivation of the sorbed amount n with the adsorption potential A (Eq. (9)):

$$\Phi = - \frac{dn}{dA} \quad (9)$$

The original equation included another division by the monolayer capacity to normalise the equation. However, this was not done in this application since many polar probe molecules do not necessarily form a monolayer on the surface.

As an example Fig. 8 shows the heterogeneity profiles for electrode graphite measured with hexane, ethanol and acetone [44]. These probe molecules represent non-specific, acidic and basic properties.

As can be seen in the figure hexane and acetone show two distinct peaks while ethanol show only one maximum in the adsorption potential range considered. The first maximum of hexane and the maximum of ethanol seem to be located at similar adsorption potentials and might represent the interaction with the same or similar energy sites. The main acetone peak is shifted to lower adsorption potentials. This suggests an interaction with lower energy sites. Additionally, some hexane and acetone molecules seem to occupy even higher energy sites (second peak). The area under the curve is related to the uptake of the different energy sites. For both acetone and hexane the lower energy sites of the graphite have a bigger population than the high-energy

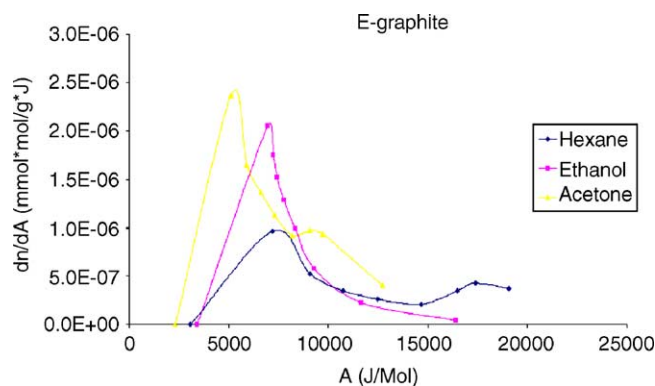


Fig. 8. Heterogeneity profiles of electrode graphite at 303 K for hexane, acetone and ethanol (taken from [44]).

sites. Similar trends were found by Papirer et al. [45] using adsorption energy distribution functions.

The adsorption potential distribution, as demonstrated above, provides important information about the surface chemistry but assumes a physisorption interaction. In some cases this assumption is not valid for polar probe molecules due to a reversible or irreversible chemisorption. In the case of a reversible chemisorption there is an enhanced adsorption potential making desorption extremely slow. Thus, no measurable peak is obtained for an elution at measurement temperature. A solution to this problem is found in a combination of IGC with thermal desorption methods. Coudhary and Sansare [29] used a combination of a continuous flow method and TPD. In their work a mixture of thiophene and carrier gas was sent through a column with copper chromite. Then they switched to pure carrier gas and ramped the temperature with a moderate heating rate (10 K/min). The result was a TPD spectrum, which showed peaks for different high energy sites on the surface.

Another approach was recently by Thielmann and Baumgarten [30]. In this work a combination of IGC and flash thermodesorption was used to achieve a separation of micropore from monolayer adsorption.

In the case of irreversible chemisorption titration methods can be applied. In a titration the same probe molecule is injected with the same concentration under identical conditions until saturation has been reached. Initially the peak area increases due to the raising saturation of the surface with the probe molecule. When the surface is completely covered with the probe molecule the peaks show a constant peak area and the amount chemisorbed can be calculated from the “missing” areas.

This method was originally developed for the determination of the metal surface area in metal/support catalysts. Gruber [31] was one of the first to use a chromatographic device for this type of experiment. He analysed the degree of dispersion of a platinum/alumina catalyst by using carbon monoxide as a probe molecule.

Another application of the titration method is for the determination of the uptake of polar organic probe molecules. Cavallaro et al. [32] measured the ethanol chemisorption on alumina.

Since these measurements are purely based on a change in peak area and not retention time they cannot be considered as chromatographic methods even though they can be carried out by a chromatograph.

3.5. Permeability and diffusion

All measurements discussed so far provide thermodynamic parameter. But IGC also offers the possibility to obtain kinetic data such as diffusion constants. The term “diffusion” is used in literature to describe both the gas phase and the diffusion into a particle. Fig. 9 illustrates the different types of diffusion processes for porous materials.

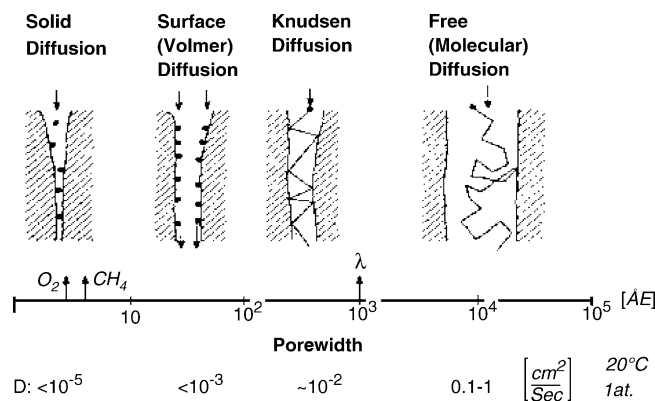


Fig. 9. Different diffusion types for gas–solid chromatography (taken from [33]).

Assuming the mean free path of the probe molecule is greater than the width of any existing pore structure of the adsorbent the diffusion is dominated by longitudinal diffusion in the gas phase. Longitudinal diffusion can be separated into two contributions: the free or molecular diffusion and the Eddy diffusion [33]. The molecular diffusion reflects the fact that the column has a particular length and diameter. Therefore, the molecules spread in both axial and longitudinal directions. The Eddy diffusion is due to the inhomogeneous particle shape or packing of the particles in the column. Therefore, the velocity of molecules through the column varies. Both effects cause a broadening of the peak. For these reasons the flow rate is an important experimental parameter because gas phase diffusion becomes more significant with decreasing flow rate.

Diffusion processes into a pore structure are usually due to solid, surface or Knudsen diffusion.

A simple theoretical treatment can be made by the Van Deemter equation (Eq. (10)) [34], which was developed for analytical chromatography but provides a reasonable description of the above-mentioned effects in the case of IGC as well.

$$H = A + \frac{B}{u} + Cu \quad (10)$$

where H is the theoretical plate height; u , linear flow rate and A , B and C constants. A represents the Eddy diffusion and, is therefore, related to the homogeneity of the column packing. The constant B represents the molecular diffusion and C is related to non-equilibrium effects such as bulk or pore diffusion.

The linear flow rate is calculated from the length L of the packed column bed and the dead-retention time t_0 . The theoretical plate height can be derived from the bed length L , the half width b and the gross retention time t_R (Eq. (11)):

$$H = \frac{L}{8 \ln 2} \left(\frac{b}{t_R} \right)^2 \quad (11)$$

Habgood and Hanlan [35] applied this approach to calculate the micropore diffusion of nitrogen and hydrocarbons in activated charcoal.

Assuming the micropore diffusion is the dominating process inside the particle and a uniform packing of particles with a narrow monomodal particle size distribution with an average diameter d the constant C is directly related to the diffusion constant D_P (Eq. (12)). k is the partition coefficient:

$$C = \left(\frac{16}{\pi}\right) \left(\frac{k}{1+k}\right) \left(\frac{d^2}{D_P}\right) \quad (12)$$

This equation represents a very general description of the relation but is applicable to various systems. More sophisticated equations are published in literature for particular adsorptive/adsorbent systems [37,38].

4. Conclusions

IGC has been shown to be a versatile tool for the characterisation of a variety of different properties of porous materials.

Especially the determination of surface energy parameters at infinite dilution but also energy distributions at finite concentration have a huge potential in the future in solving manufacturing and processing related problems.

Acknowledgements

I would like to thank my colleagues at Surface Measurement Systems Dr Daniel Burnett, Dr Majid Naderi as well as Mrs Manaswini Acharya and Mr Armando Garcia for their constant support and excellent work.

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