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Extension of the IGC analytical techniques to flat solid surfaces: feasibility study
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✍ Abstract

The aim of the present work is to demonstrate that, using a simple device defining a chromatographic path between 2 plates of glass, it becomes possible to extend the classical inverse gas chromatography (IGC) technique, commonly applied up to now to the sole powders or fibers, to the study of flat solid surfaces.

The potential of interaction of 3 glass plates, modified by a mineral coating, is assessed through IGC measurements, in infinite dilution conditions, whereas IGC at finite concentration conditions gives access to the relative surface area of the studied samples and to their surface energetic heterogeneity. This study shows that an aging process increases both the relative surface area and the energetic heterogeneity of the surface coating.

Keywords

Inverse gas chromatography, Flat surfaces, Glass, Relative surface area, Surface energetic heterogeneity

Introduction

The analytical inverse gas chromatography (IGC) techniques were extensively applied to the study of the surface properties of powders or fibers packed into a GC column[1]. So far, it was not to apply IGC to planar surfaces. The determination of the interaction potential of flat surfaces was made by wettability based on through liquid contact angle measurements: a rather macroscopic technique.

The aim of the present work is to demonstrate that IGC may be simply extended to flat glass surfaces coated with colloidal particles.

Experimental

Experimental device

The extension of IGC techniques from column to flat surfaces is based on a patented experimental device [2] in which the carrier gas is forced to flow between the two plates made of the solid of interest. The chromatographic path is designed using a Teflon sheet in which the wanted path is cut. The principle of this device is depicted on figure 1.
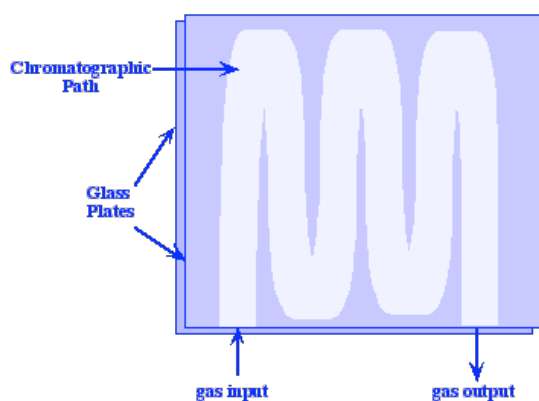

Figure 1 : *Schematic representation of the IGC device for the surface properties measurements of solid plates.*

In this instance, the analysis is performed on 2 plates that are 210 mm long and 185 mm large. The geometrical surface of the path is equal to 380 ± 1 cm^2. The input and the output of the carrier gas are placed on the edge of the device using a convenient connecting system. The other characteristics of the chromatographic measurement system chosen starting from the results of our previous work done on empty stainless steel tubing[3].

Samples

Three glass plates, samples A, B and C, were submitted to the IGC analysis. Their surface was coated with a thin layer of a mineral colloidal material according to an industrial process. Glass B plates correspond to glass A plates submitted to an aging treatment. Glass C plates contain present a very thin coating. The plates were conditioned during 20 h, at 60°C, under a helium gas flow of about 5 cm^3/min, in the chromatograph oven. Obviously, the pressure drop at the entrance of such a device is very low and the James Martin correction for the gas compressibility becomes negligible. The same value for the flow rate was retained for all measurements.

IGC measurements

IGC experiments at infinite dilution conditions (injecting traces of solutes or molecular probes) and finite concentration conditions (injecting measurable amounts of solutes) were performed.

The IGC measurements, at infinite dilution conditions, were performed only at one temperature (30°C).

Under these conditions, the following measurements were made:

- Dispersive component of the surface energy (γ_s^d) using n-alkane probes.
- Specific interactions level of the surface by injecting different polar probes.

The IGC measurements, at finite concentration conditions, were performed only at one temperature (30°C).

Under these conditions, the following measurements were made, using n-pentanol or n-butanol probes:

- Desorption isotherms.
- Specific surface area (BET method).
- Adsorption Energy Distribution Functions.

Results

IGC in infinite dilution conditions (IGC-ID)

Figures 2 and 3 display the chromatograms obtained on glass plates A and B, using n-alkane and aromatic molecules as probes.

These chromatograms look like those obtained for instance on a chromatographic column, having 20 cm length and 2 mm inner diameter, filled with pyrogenic silica particles.
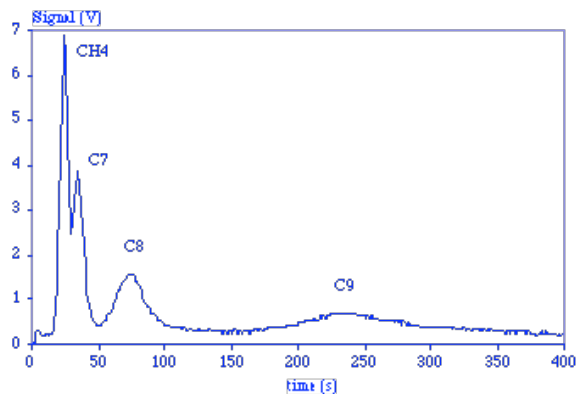
Figure 2 : *Chromatogram (IGC-ID) obtained for glass plates A using n-heptane, n-octane and n-nonane probes, at 30°C.*
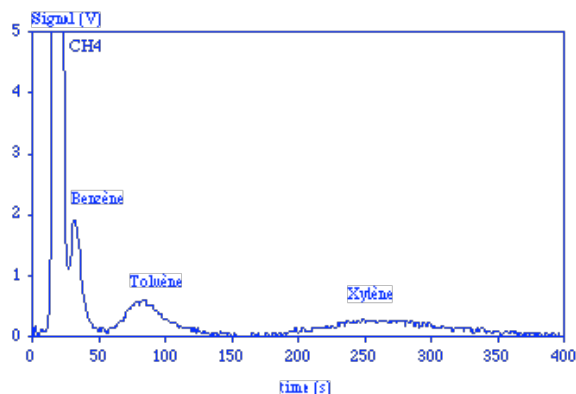

Figure 3 : *Chromatogram (IGC-ID) obtained on glass plates A using benzene, toluene and xylene probes, at 30°C.*

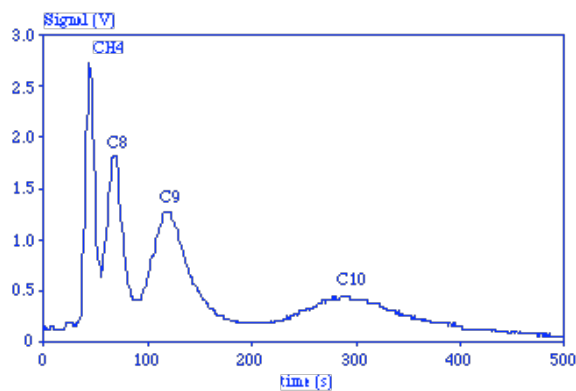Very similar chromatograms were also acquired on glass B plates as it is shown on figures 4 and 5.

Figure 4 : *Chromatogram (IGC-ID) obtained for glass plates B using n-heptane, n-octane and n-nonane probes, at 30°C.*
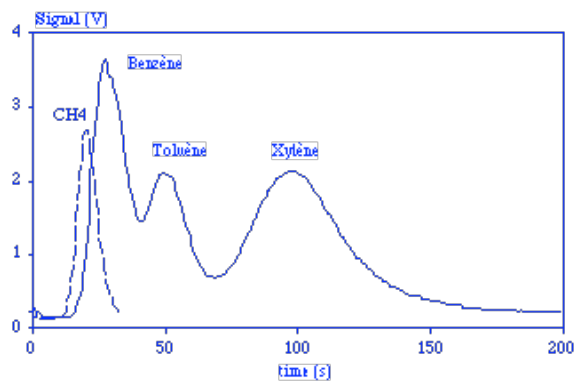

Figure 5 : *Chromatogram (IGC-ID) obtained on glass plates B using benzene, toluene and xylene probes, at 30°C.*

The comparison of those chromatograms shows that the glass plates B exhibit a much lower potential of interaction (shorter retention times) than do glass plates A.

The surface energy of a solid is commonly considered as a sum of 2 components: the dispersive component corresponding to the sole Van der Waals interactions and the so called specific component taking into account all other types of interactions (polar, acid-base…).

The dispersive component (or non-specific) of the surface energy (γ_s^d) was calculated according to the Dorris and Gray approach[4]. From the slope of the straight line, obtained when plotting the logarithm of the retention time or retention volume *V* (proportional to the variation of free energy of adsorption) versus the number of Carbon atoms of the n-alkanes, the dispersive component of the surface free energy is calculated applying the following equation:

$$\gamma_s^d = \frac{\left(\Delta G_{CH2}\right)^2}{4N^2 a_{CH2}^2 \gamma_{CH2}} \qquad \text{[Eq. 1]}$$

where N is Avogadro's number, a_{CH2} is the area covered by one adsorbed methylene group (0.06 nm²), and γ_{CH2} is the surface energy (in mJ/m²) of a solid made of methylene groups, i.e., polyethylene, $\gamma_{CH2} = 35.6 + 0.058 (293 - T)$. ΔG_{CH2} is obtained from the slope of the straight line (see figure 6), namely:

$$\Delta G_{CH2} = -RT \ln \frac{V_{n(n)}}{V_{n(n+1)}} \qquad \text{[Eq. 2]}$$

The specific interaction potential of the surface may be assessed by injection of polar probes. When injecting a polar probe, one obviously records only one peak, per probe and its retention time is, of course, related to both London and specific interactions. Hence, a procedure has to be established to separate the two different contributions. Plotting -ΔG_a , (or RT.Ln(Vn)) versus a molecular parameter related to the polarizability of the probe, here the topological parameter χ_t proposed by Brendlé and Papirer[5] permits to perform this separation. All representative points of the n-alkane probes fall on a line, whereas those corresponding to polar probes are located above that line (higher retention volumes or higher interaction capacity).

By definition, the specific interaction parameter, ISP, is given by the departure of the representative point of the polar probe from the alkane line. In other words, ISP is equal to the increment of free enthalpy related to the specific interaction capacity of the probe. In the case of a homologous solutes series, like aromatic probes such as benzene, toluene and xylene, the ISP value does not vary significantly with the increasing number of methyl groups. Hence, only the mean value ISP^{arom}, equal to the average value of the benzene, toluene and xylene ISP is retained.
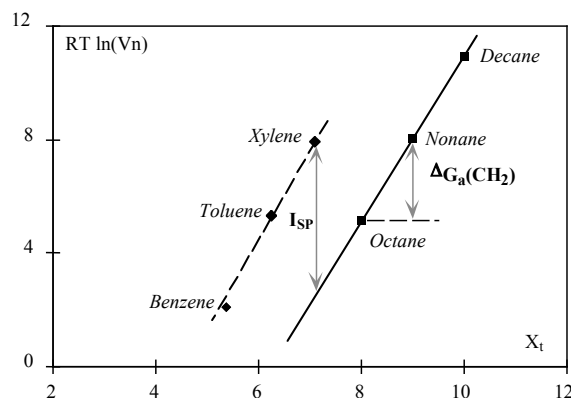

Figure 6 : *Determination of γ_s^d and benzene ISP values, by IGC-ID, on glass B sample. (Xt of n-alkane probes are equal to their number of carbon atoms).*

The γ_s^d and benzene ISP values, measured on the glass plates, are reported in the table 1.

These values indicate the higher potential of interaction of the glass A surface in comparison with the two other glass samples. Obviously, the aging (glass B) leads to a significant decrease of both non-specific and specific potentials of interaction. Generally, a freshly prepared glass surface exhibits meta-stable structures having a high potential of interaction, whereas aging leads to a

rearrangement of the surface layer induced by a minimization of the surface energy and, hence to a diminution of the potential of interaction. This may be attributed to cation migration on the glass surface. This remains as an hypothesis since we do not have any supplementary information provided by another analytical technique.

Table 1 : *Dispersive Component* γ_s^d *and specific interaction parameter* ISP^{arom} *of A, B and C glass plates.*

Samples	γ_s^d	ISP^{arom}
A	107	12,2
B	46	5,3
C	39	non measurable

IGC, in finite concentration conditions, may provide some additional information concerning the actual interacting surface area (comparing with the geometrical surface) area and the surface energetic heterogeneity.

IGC in finite concentration conditions (IGC-FC)

On the contrary of the IGC-ID conditions, a finite volume of liquid probe is injected into the chromatographic device. Here, the injected volume was equal to about 0.2µl. Alkane or aromatic probes are not interactive enough to obtain exploitable IGC-FC chromatograms. Alcohol probes, such as n-butanol and n-pentanol, are definitely more interactive and therefore more appropriate for the surface examination of the glass plates. They are also more sensitive to the variability of the surface functionality because of their ability to exchange specific interaction with the surface hydroxyl groups through hydrogen bridges.

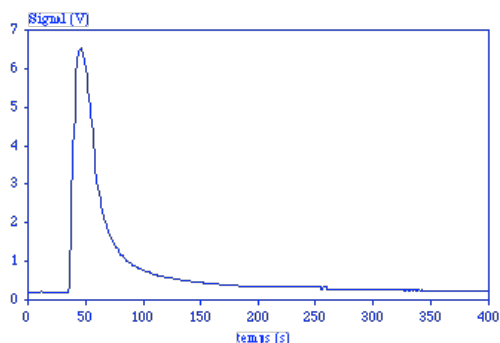An IGC-FC chromatogram of n-pentanol probe, on glass A sample, is displayed on figure 7.

Figure 7 : *IGC-FC chromatogram of n-pentanol probe on glass sample A, acquired at 30°C (Injected volume: 0.25 µl).*

Different IGC methods for the determination of the adsorption isotherms have been reviewed by Conder[6]. The simplest one, "the elution characteristic point method" (ECP) allows the acquisition of the desorption isotherm from a unique chromatographic experiment. Using this method, the first derivative of the adsorption isotherm can be readily calculated starting from the retention times and the signal heights of characteristic points taken on the diffuse descending front of the chromatogram, according to equation 3:

$$\left(\frac{\partial N}{\partial P}\right) = \frac{J\,D\,t'_r}{m\,RT} \qquad \text{[Eq. 3]}$$

where, N is the number of absorbed molecules, P the pressure of the probe at the output of the column, t'_r the net retention time of a characteristic point on the rear diffuse profile of the chromatogram, J the James and Martin's coefficient, D the output flow rate and m the mass of adsorbent.

According to the ECP approach[6], the isotherm of desorption can be readily calculated. The desorption isotherm of n-pentanol, on glass A, is shown on figure 8.
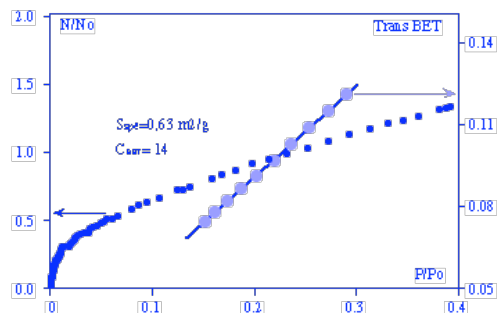

Figure 8 : *Desorption isotherm of n-pentanol, on the glass sample A, measured à 30°C and its BET transform.*

Applying the BET theory to this isotherm, allows to evaluate the "actual" or interacting surface area developed by the glass surface. The BET transform is displayed on figure 7. Knowing the geometrical surface of the analyzed sample corresponding to the surface area delimited by the intercalated cut Teflon sheet, on can calculate the relative surface area (Srel), which is equal to the ratio of the measured surface area on the geometrical area of measurement. The main characteristics of the isotherm of desorption of n-pentanol on glass A, B and C samples are gathered in table 2.

Table 2 : *Main characteristics of the isotherm of desorption of n-pentanol and surface roughness R of the glass plates A and B, measured using IGC-FC.*

Samples	S_{BET} (m²)*	Srel**	C_{BET}
A	0.63	16	14
B	1.63	43	15
C	1.35	34	6.4

* S_{BET} *is the surface area developed by the geometrical 380 cm² of the tested glass area.*
** *Srel is equal to the ratio between the actual interacting area and the geometrical area (380 cm², in the present study).*

It is seen that those samples develop an "actual" surface area much higher than the geometrical area. Moreover, the comparison of sample A with sample B proves that the aging process induces an important increase of the surface porosity. Finally, sample C develops an intermediate surface area. According to the values of the BET constants, the aging process has quite no influence; only sample C exhibits a lower value than do the other 2 samples.

Furthermore, IGC-FC gives access to the surface energetic heterogeneity using the Rudzinski-Jagiello approach[7], modified by Balard[8].

Assessment of the surface energetic heterogeneity

From the shape analysis of the desorption isotherm, one can appreciate the surface energetic heterogeneity of the glass plates. For such an analysis, a physical adsorption model is required. Generally, one admits that the global isotherm may be considered as a sum of local isotherms of adsorption on isoenergetic domains[7]. Then, the surface heterogeneity is described by a distribution function corresponding to the relative abundance of each type of domain having the same characteristic energy of interaction (ε). This characteristic energy is related to the pressure of measurement[7] by equation 4:

$$K = C \times 10^4 (MT)^{1/2} \qquad \text{[Eq. 4]}$$

where M is the probe molecular weight and T is the experimental temperature (K) and C a constant depending of the pressure unit: C=1.76104 when the pressure is expressed in torr and : C=2.346103 when the pressure is expressed in kPa.

Taking into account the previous physical model, the general equation, which describes the physical adsorption on heterogeneous solid surfaces, is usually written in the following integral form:

$$N(T,P) = N_0 \int_{\Omega} \theta(\varepsilon,T,P) \; \chi(\varepsilon)d\varepsilon \qquad \text{[Eq. 5]}$$

where $N(T,P)$ is the number of molecules adsorbed at pressure P and temperature T of measurement, N_0 is the number of molecules corresponding to the formation of a monolayer, $\theta(\varepsilon,T,P)$ is the local isotherm (generally the Frumkin, Fowler, Guggenheim's isotherm) corresponding to adsorption sites having the same characteristic adsorption energy ε, $\chi(\varepsilon)$ is the so-called adsorption energy distribution function (DF) describing the energies which exist at the gas-solid interface and Ω is the physical domain of the adsorption energy.

From a mathematical point of view, solving the former integral equation is not a trivial task because it has no general solution, except when one adopts a step function as local isotherm that says the "condensation approximation". The condensation approximation supposes that the sites of adsorption of given energy are unoccupied below a characteristic pressure and entirely occupied above it. The distribution function for the condensation approximation (DFCA) is directly related to the first derivative of the isotherm corrected for the multilayer adsorption, according to equation 6:

$$\chi_{CA}(\varepsilon) = \frac{P'}{RT} \frac{\partial}{\partial P'} \left[\frac{N'(P')}{N_0} \right] \qquad \text{[Eq. 6]}$$

where : N' and P' are respectively the amount of adsorbed probe and the equilibrium pressure of the probe corrected for the multilayer adsorption, N_0 is the amount of adsorbate corresponding to the monolayer formation, R the universal gas constant for an ideal gas and T the absolute temperature at which the measurement is performed.

The first derivative of the isotherm corrected for the multi-layer adsorption[9] (experimental isotherm of type II) is related to the experimental isotherm and its first derivative by equation 7:

$$\frac{\partial N'}{\partial p'} = (1-x)^3 \frac{\partial N}{\partial p} - (1-x)^2 \frac{N}{P_0} \qquad \text{[Eq. 7]}$$

The experimental distribution function for the condensation approximation of the adsorption energies of n-pentanol on glass sample A is shown on figure 9.
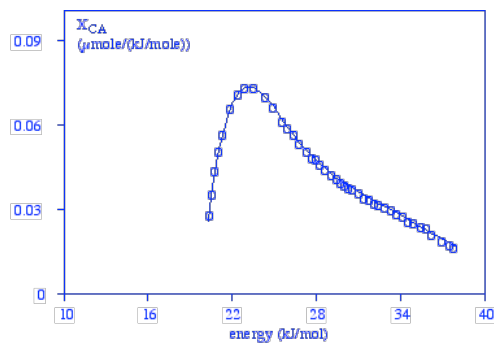
Figure 9 : *Adsorption energies distribution function, for the condensation approximation, of n-pentanol (injected volume: 0.25 µl), measured at 30°C, on glass A.*

The approximation is all the better as the temperature of measurement approaches the absolute zero. In the usual IGC measurements conditions, at room temperature and above room temperature, this approximation fails completely and it becomes necessary to use other approximated forms of the local isotherm. Among them, for Langmuir local isotherms, the extended Rudzinski et al method[7] allows the computation of the actual distribution function (DFRJ) from a limited development of the even derivatives of the DFCA, according to equation 8:

$$\chi(\varepsilon) = \sum_{j=0}^{+\infty} (RT)^{2j} \, b_{2j} \, \dot{\chi}_{CA}^{(2j)}(\varepsilon) \qquad \text{[Eq. 8]}$$

$$\text{with } b_0 = 1 \quad \text{and} \quad b_{2j} = (-1)^j \frac{\pi^{2j}}{(2j+1)!}$$

The use of a signal treatment method, based on Fourier's transforms, allows a simple way for the filtration of the isotherm data (elimination of the experimental noise contribution). The remarkable robustness of this new approach, versus noise and irregular sampling, was carefully tested and the energetic surface heterogeneity of a series of solids [10, 11, and 12] was evaluated.

The distribution functions (RJ4 approximation, j equal up to 2 in equation 8) of the adsorption energies of butanol and pentanol measured at 30°C, on glass A, are shown on figure 10.
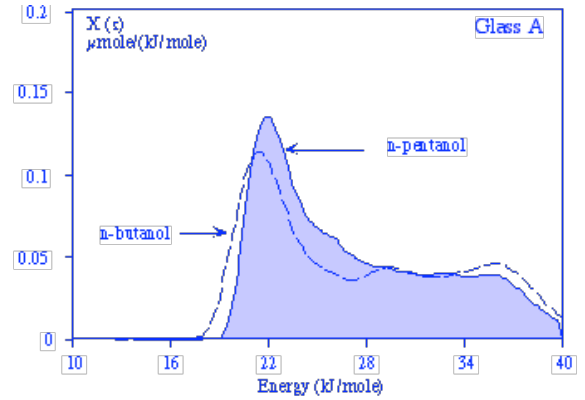
Figure 10 : *Distribution functions (RJ4 approximation) of the adsorption energies of butanol and pentanol, (injected volumes: 0.25 µl), measured at 30°C, on glass A.*

The two distribution functions exhibit very similar shapes proving the reproducibility of both the IGC acquisition of the isotherm adsorption first derivative and the robustness of the calculation method of the distribution functions. The shift observed between the n-butanol and n-pentanol distribution functions is attributed to the increasing length of the alkyl chain. These distribution functions testify the strong energetic heterogeneity of the glass surface. According to the interpretation given for the distribution functions of the isopropanol adsorption energies on fumed silica, the main peak around 22 kJ may be attributed to domains quite free of silanol groups, whereas the important tail is certainly related to a high silanol local density and/or cations.

The distribution function of the adsorption energies of n-pentanol on glass B is depicted on figure 11, the distribution function established on glass A being taken as reference.

Obviously, the aging process increases the surface heterogeneity as well as the specific surface area as mentioned above. The peak around 22kJ/mole is slightly shifted toward the higher energies and becomes sharper, correlatively the tail is extended towards the high adsorption energies, indicating a strong change of the colloidal layer structure.
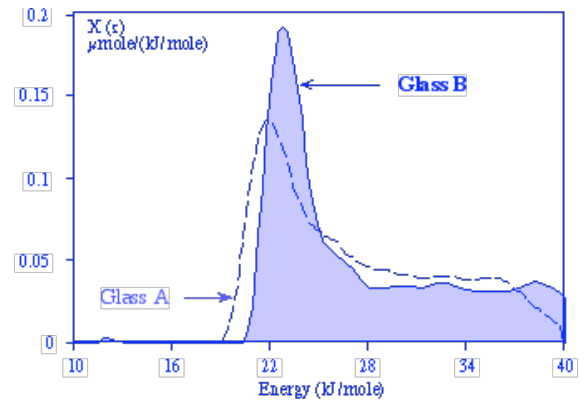
Figure 11 : *Distribution function (RJ4 approximation) of the adsorption energies of n-pentanol, measured at 30°C, on glass B. The distribution function of glass A sample is given for the sake of comparison..*

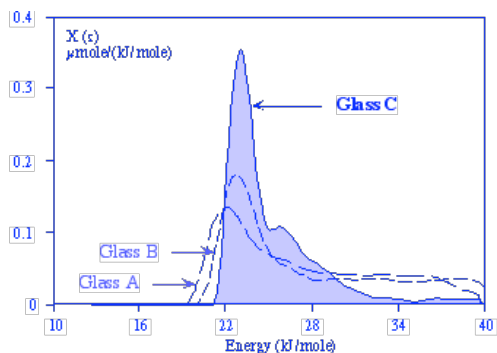Finally, the adsorption energies distribution function of glass C is shown on figure 12.

Figure 12 : *Distribution function for the RJ4 approximation of the adsorption energies of n-pentanol, measured at 30°C, on glass C. The distribution functions of glasses A and B are given for the sake of comparison.*

Obviously, the glass C sample exhibits a much lower surface heterogeneity than do the A and B sample. The maximum of the distribution function is clearly shifted toward the higher energies. Glass C is the less modified glass sample. It could be possible that the coverage of this glass surface is only « partial », leaving part of the original glass surface accessible to the probe.

Conclusion

These first experiments demonstrate clearly that the extension of the IGC techniques, from their classical application domains (powders and fibers essentially), to flat solid surfaces is indeed possible. Hence, the potentiality of the IGC measurements for the assessment of surface potential of interaction and energetic heterogeneity determination is now opened to numerous other domains. For example, the new applications of IGC demonstrated above could be most appropriate for the control and tailoring of solid surfaces in order to solve problems relevant to adhesion (glass metals, polymers…), industrial production, control of the quality and of the aging coatings to cite just a few of them.

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