



The Characterisation of Surface Area and Surface Adsorption Potential Heterogeneity Profiles of Hair by Inverse Gas Chromatography

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In the present paper the surface areas and adsorption potential distributions of nine different hair samples have been determined by Inverse Gas Chromatography (IGC SEA). The distribution function reflects the energetic heterogeneity profile of a surface and provides interesting information on the nature and population of different surface sites. In this study IGC SEA is shown to be a fast and accurate technique for the determination of these distribution functions.

Introduction

Recent work on hair has shown that IGC SEA is a useful technique for the determination of changes occurring on the hair surface during treatment such as UV exposure or chemical bleaching [1]. This study was carried out at infinite dilution where small differences between materials can be detected due to the interaction of the probe molecule with the highest energy sites on the surface. Although this method is extremely sensitive, it provides only information about the high-energy sites. For many applications it is desirable to study the entire surface and therefore to include also lower energy sites. This is particularly useful for the understanding of residues left on the hair surface by shampoos and conditioners.

The scope of this study is the investigation of the surface heterogeneity of hair samples subjected to bleaching, perming and conditioning by using water and hexane as probe molecules.

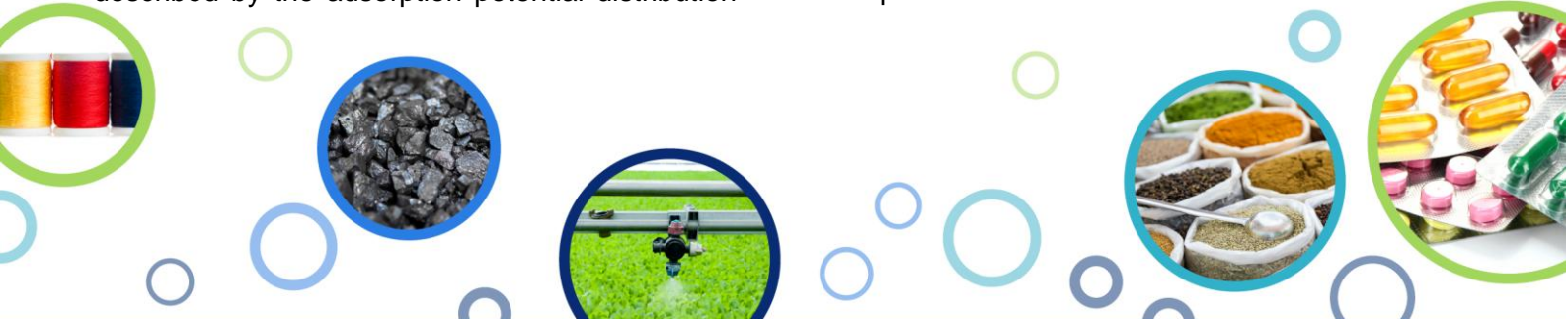
Theory

The energetic heterogeneity of a surface can be described by the adsorption potential distribution

[2]. This can easily be calculated from the sorption isotherm. The isotherm can be derived from an IGC SEA pulse or frontal measurement by a variation of the probe molecule concentration. In this case the retention time obtained is converted into the retention volume and the height of the peak/front into the partial pressure. 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 provides the desorption isotherm in either case. A detailed description of this calculation procedure is given in [3]. In order to obtain the distribution function the partial pressures are converted into the adsorption potential A according to Equation 1.

$$A = R \cdot T \cdot \ln\left(\frac{p_0}{p}\right) \quad (1)$$

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



The distribution parameter Φ represents the first derivative of the sorbed amount n with respect to the adsorption potential (Equation 2).

$$\Phi = -\frac{dn}{dA} \quad (2)$$

The original equation [2] included another division by the monolayer capacity to normalise the equation. However, this was not done in this application since newer research shows that especially polar probe molecules do not necessarily form a monolayer on the surface [4]. An extensive discussion on different calculation methods can be found in [5].

Method

Nine different hair samples have been investigated. The samples were prepared and supplied by TRI, Princeton. Table 1 shows the details of the applied surface treatment. CTAB is cetyl trimethylammonium bromide, and JR400 is quaternized cellulose derivative, polyquart 10.

Table 1. Description of the hair samples used in this study.

Hair Samples		
Sample 1	no treatment	no conditioner
Sample 2	no treatment	CTAB
Sample 3	no treatment	JR400
Sample 4	Bleached	no conditioner
Sample 5	Bleached	CTAB
Sample 6	Bleached	JR400
Sample 7	bleached and permed	no conditioner
Sample 8	bleached and permed	CTAB
Sample 9	bleached and permed	JR400

All sorption experiments were carried out on an SMS-iGC 2000. The hair was packed into standard columns (0.2 and 0.4 cm ID, 30 cm in length). For all nine samples the isotherms have been determined. Measurements were performed

with hexane (dispersive probe) and water (polar probe). Prior to the measurements a pre-treatment was carried out for 3 h at 303 K to remove physisorbed water from the surface. For experiment-to-experiment reproducibilities another purge of 60 min was carried out between measurements.

After the pre-treatment procedure pulse injections were performed by a 0.25 ml gas loop at 303 K. For a peak maximum experiment measurements were undertaken between 0.05 and 0.95 p/p_0 in the case of hexane and 0.05 and 0.65 p/p_0 injection concentration in the case of water. Calculations were performed using the SMS iGC Standard Analysis Software and the Advanced Analysis Software v1.2.

Results

Figure 1 shows the pulse isotherms for a multiple injection experiment (Peak Maximum) with hexane on different hair samples at 303 K.

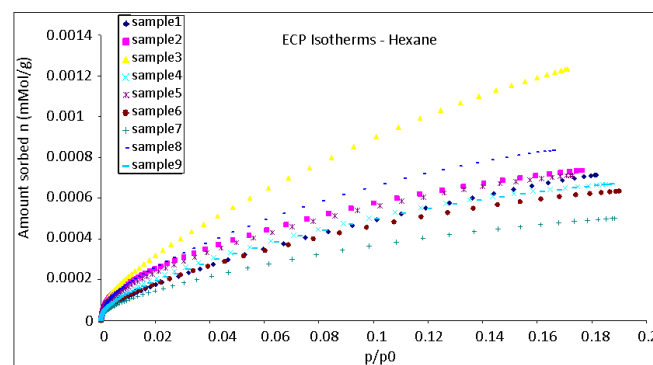


Figure 1. ECP isotherms of hexane on different hair samples at 303 K.

The interaction with hexane describes a dispersive interaction. Therefore, there is no surprise that the sorption isotherms are reflecting a typical type II mechanism.

Such isotherms can be used to compute the surface area by applying the BET method. The calculation procedure is describe elsewhere [3].

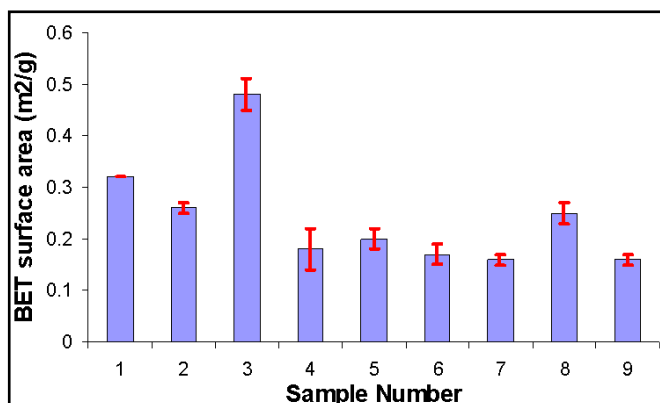


Figure 2. Surface areas (with error bars) for different hair samples measured at 303 K with hexane.

The BET surface areas determined from these IGC SEA measurements (Peak Maximum method) with hexane are shown in Figure 2 together with the error bars of the experiment.

For many of the samples (4,5,6,7 and 9) differences are in the error margin of the experimental determination. However, it is obvious that sample 3 has by far the highest surface area. The surface areas of samples 1 and 2 are similar and lower than for sample 3 but significantly higher than for 4,5,6,7 and 9. Sample 8 has a surface area similar to sample 1 and 2.

As a trend it can be concluded that surface areas of samples 4-9 are lower than that of the untreated hair. This can be explained by the fact that a number of dispersive sites have been substituted by polar sites. Such chemical treatment makes the surface more polar and the affinity to hexane decreases.

The enhanced surface area of sample 3, compared to sample 1 and 2 may be due to the nature of the conditioner. JR400 is a quarternised cellulose derivative with butyl side-chains. Such a surfactant increases the affinity to hexane. CTAB on the other hand, which is cetyl triethylammoniumbromide, does not cause such an increase, but eventually causes even a small decrease in the interaction with hexane. Another explanation could be a deposition of the JR400 on the fibre surface as an uneven and relatively thick film. This does not occur on treated fibres since the polymer films on these high energy surfaces are rather smooth and almost indistinguishable from the untreated fibres. This assumption is supported by SEM pictures taken recently [6].

The BET concept for the determination of the surface area assumes a homogeneous surface structure. This, however, is not appropriate for many systems as they show a strong variation of energy sites on the surface. In such cases the heterogeneity profile can give a more detailed picture since it provides the distribution of the adsorption potential.

As explained above hexane can only describe the dispersive interactions with the hair samples. A polar probe molecule such as water is expected to reveal more significant differences between the samples and their sorption behaviour. Figure 3 shows a comparison of the water isotherms for the different hair samples.

The partial pressure range considered is much lower than for hexane due to the strong interaction of water with the hair surface.

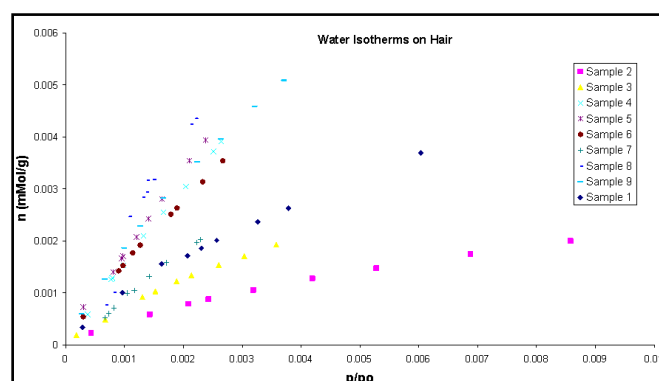


Figure 3. Peak Maximum isotherms of water for different hair samples at 303 K.

The surface heterogeneity profiles (adsorption potential distributions) are plotted in Figure 4.

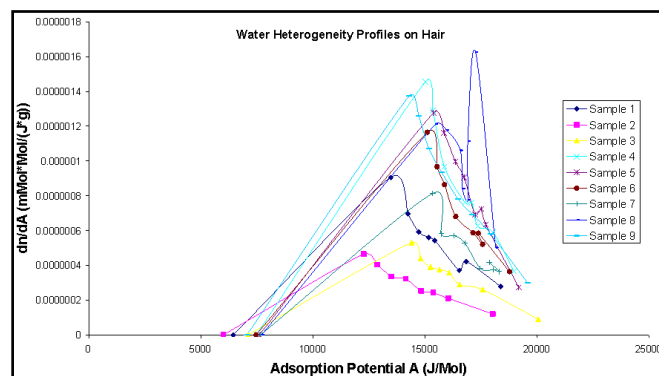


Figure 4. Adsorption potential heterogeneity profiles of different hair samples at 303 K measured with water



The adsorption potential distributions show very significant differences in the uptake and the energy level for the hair samples and how they are affected by treatments. All curves have a main maximum and one or more shoulders. Each maximum represents an energy level of a certain adsorption site for water.

One can clearly identify at least seven different energy centres at 12300, 13500, 14400, 15000, 15400, 16300 and 17250 J/Mol. The area under each curve corresponds to the uptake and thus, to the population of sites of that type.

Comparing the curves for the samples without conditioner (1, 4 and 7) it can be seen that bleaching and perming causes a shift to higher adsorption potentials indicating an increase the number of high energy sites on the surface of hair. The surface of hair is covered by cuticle cells which are covered by a lipid layer and therefore, is of low energy. This is receptive to the adsorption of nonpolar molecules like hexane. Grooming procedures damage the surface of these cells by eliminating the lipid layer and therefore, increase the number of interacting sites.

On the untreated hair, treatment with conditioners appears to decrease the number of hydrophilic sites. This can clearly be seen by the lower water uptake of sample 2 and 3 compared to sample 1 and is most likely due to monolayer adsorption of conditioners, especially CTAB, through salt linkages. This results in a surface populated by hydrophobic moieties. Sample 2, however, shows also a decrease in the mean adsorption potential, which indicates a reduction in the high energy sites due to the treatment with CTAB.

A comparison of samples 4, 5 and 6 shows that bleaching leads to a large increase in the number of high energy sites and the distribution is moving up and to the right. This is due to the generation of acidic sites which adsorb a lot of conditioner. The adsorption of CTAB (sample 5) leads to an increase in the number of high energy sites. This may be because of bilayer adsorption through hydrophobic bonding which leaves the positive charges of the quaternary groups on the surface. The effect of JR 400 (sample 6) is similar to that

of the untreated hair, although the water uptake is significantly higher after the bleaching procedure.

Conditioners also adsorb strongly on hair which was bleached and permed as can be seen in a comparison of samples 7, 8 and 9. This is especially true for CTAB which penetrates into the hair. This may be responsible for the sharp high energy shoulder at 17250 J/Mol (sample 8). It is very likely that this involves the internal surface of the fibre. Behaviour of JR 400 (sample 9) is again similar to that observed in the case of untreated and bleached hair. Adsorption of this polymeric conditioner on the surface does not seem to increase the number of high energy sites. However, once again perming and bleaching increases the water uptake.

These results clearly show the benefits of analysing the surface of hair by IGC SEA. Effect of chemical treatments and concomitant changes in surface energy can be followed by this method. Changes in the nature of the surface by adsorption of conditioners can also be discerned. The method is sensitive enough to be able to identify the effects of surfactant deposits left by shampoos and other haircare products.



Conclusion

Surface adsorption potential heterogeneity profiles for water and BET surface areas have been determined on nine different treated hair samples. IGC SEA was proven as a fast and sensitive technique for the identification of differences in the water uptake due to changes in the surface structure of hair.

BET surfaces show only small differences between samples as they represent only dispersive interactions. They cannot reflect any energetic changes on the hair surface due to different treatment. However, such effects can be studied by determining surface heterogeneity profiles based on the interaction with water. Preliminary work reported here clearly indicates that the deposition of conditioner residues can be studied by this method.

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