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iGC SEA
Application
Note 210

Investigation of the Influence of Bleaching Conditions on Surface Properties of Standard Hair Samples by Inverse Gas Chromatography

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The surface energy is a useful parameter describing the energetic properties of the surface of a solid sample. It can be determined in a fast and accurate way by inverse gas chromatography (IGC SEA). This paper describes the application of this approach for the investigation of how different bleaching conditions can cause changes on the surface of standard hair samples.

Introduction

The surface energy is an important parameter for the characterisation of surface properties. It can provide a useful picture of the energetic situation on the surface and shows therefore a strong correlation with various macroscopic properties. For instance the dispersive component of the surface energy is a useful tool to follow changes on oxide surfaces caused by temperature treatment [1] or to highlight batch-to-batch variation in industrial production [2]. The polar interaction parameter can provide useful information on acidity/basicity or particular surface groups.

An easy way to study such effects is the use of dynamic methods. IGC SEA is a particularly suitable technique that allows a fast and accurate determination of the surface energy, either the dispersive component or the interaction with polar probes.

In the current study different pre-treated hair samples were investigated to obtain a correlation between experimental data and treatment conditions.

The basic component in hair is keratin, a skleroprotein. All keratins contain a high amount of cystine, which makes an important contribution to stabilisation due to its sulphur content. Other important amino acids in keratin are leucine, serine, arginine, proline, glutaminic acid and asparic acid. This structure causes the slightly acidic nature of the hair surface.

The hair shaft can be devided into three different layers (from the outside to the inside): the cuticula, the cortex (macrofibrils) and the medulla (corticle cells). The hair color is caused by the number and composition of the pigments in the corticle cells and the macrofibrils. The effect of bleaching agents and exposure to light is due to the oxidative destruction of the pigments in the cortex and the medulla [3]. Although this happens in the inner structure of the hair the surface is also affected by this treatment. For this reason various pre-treatments cause detectable changes on the surface.

Theory

In an IGC SEA pulse measurement an injection of a certain amount of vapour is made. This pulse is transported by the carrier gas, which for the SMS-*iGC SEA* is helium, through the GC to the column. The amount adsorbed in the column is eluted by the carrier gas.

Studies were carried out in the infinite dilution range (Henry range). In range only interaction

with the higher energy sites on the surface occur, which makes energetic measurements extremely sensitive to small differences between samples.

Due to the linear shape of the Henry isotherm peaks are symmetrical (Gaussian) and the retention volume can be calculated from the retention time at the peak maximum. The net retention volumes V^0_R are computed using Equation 1.

$$V_R^0 = j/m\cdot F\cdot(t_R - t_0)\cdot\frac{T}{273.15} \qquad (1),$$

where T is the column temperature, m is the sample mass, F is the exit flow rate at 1 atm and 273.15K, t_R is the 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 relation between the retention volume and free energy of desorption ΔG is given by Equation 2.

$$\Delta G^0 = RT \ln V_R^0 + K \qquad (2),$$

where R is the gas constant and K is a constant depending on the chosen reference state (De Boer or Kemball/Rideal) [4]. Moreover ΔG is related to the energy of adhesion W_A (between probe molecule and solid) by Equation 3 (as an approximation).

$$\Delta G^0 = N_A * a * W_A \qquad (3),$$

where a is the cross sectional area of the adsorbate and N_A the Avogadro constant.

According to Fowkes [4] W_A can be split into two terms (Equation 4):

$$W_A = W_A^D + W_A^S \qquad (4),$$

with W_A^D denoting the van der Waals forces and W_A^S the specific, mainly polar interactions. Subsequently the retention volume is a measure for both components. In the case of dispersive interactions W_A is given by Equation 5.

$$W_A = 2(\gamma_S^D * \gamma_L^D)^{1/2} \qquad (5),$$

with γ_S^D and γ_L^D as the surface tension of the adsorbent and the adsorbate.

Two methods are commonly described in literature to calculate γ_S^D which is the dispersive component of the solid surface energy. The method of Schultz et al [4] uses a plot of ΔG versus $a(\gamma_L^D)^{1/2}$ for a series of alkanes. Combining Equations 3,4 and 5 leads to:

$$RT \ln V_R^0 = 2N_A\left(\gamma_S^D\right)^{1/2} a\left(\gamma_L^D\right)^{1/2} + const. \qquad (6).$$

Alternative methods are described in [5,6,7,8].

Method

Each standard hair sample was packed in a column with 30 cm length and a 4 mm ID. Standard hair samples were prepared and supplied by TRI, Princeton. Three different types of samples were provided: an untreated one, a 60 min chemical bleached and a 74 h UV treated material.

All sorption experiments were carried out on an SMS-iGC 2000. Measurements of the dispersive interaction were made with 4% p/p_0 heptadecane, hexadecane, tetradecane, hexanol and butyl acetate at 303 K (all solvents HPLC grade) and 10 ml/min. A pretreatment was made for 5 h at 303 K, 0% RH. Measurements were carried out twice on each column in order to investigate the experiment-to-experiment reproducibility.

Results

Figure 1 shows a comparison of surface energy plots of the three different samples.

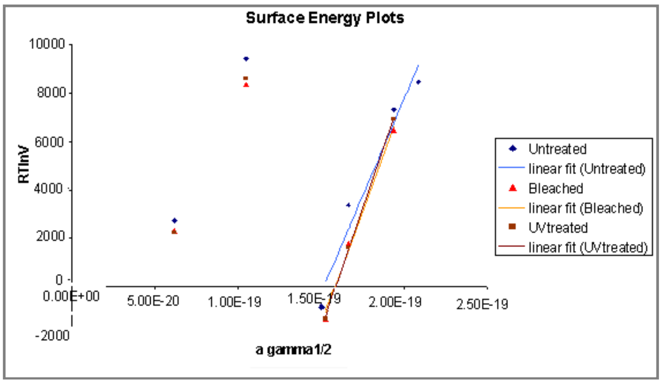

Figure 1. Alkane line (tridecane to heptadecane) and linear fit for a measurement at 30°C.

The calculation of the surface energy was made according to Schultz et al [4] by the SMS-iGC SEA analysis software (v1.1). The obtained values for all columns are listed in Table 1.

Table 1. Experimental obtained dispersive surface energies and specific free energies.

Column	ΔG [kJ/Mol] (1-Hexanol)	ΔG [kJ/Mol] (Butyl acetate)	Dispersive Surface energy $[mJ/m^2]$
Untreated	16.929	17.148	17.76*
Untreated	-	-	19.67*
Chem. Bleached (60 min)	18.591	20.685	24.78**
Chem. Bleached (60 min)	18.697	20.944	25.44**
UV treated (74 h)	19.521	21.827	28.03**
UV treated (74 h)	19.619	21.785	28.06**

* based on a fit of 4 points

** based on a fit of 3 points

The reproducibility in the same column for surface energy is excellent for the UV treated hair (0.07 % deviation) and for the bleached sample (1.31 % deviation). The reproducibility for the untreated material (5.12 % deviation) is not as good and the deviation is significantly larger than the usual expected value of approximately 2-3 %. This is due to the very weak interaction of hair samples with organic vapours, which gives only small differences in retention time to methane. Therefore these data have a higher error.

The average value of all measurements can be found in Table 2. Moreover a comparison is done with wettability data [9].

Table 2. Experimental obtained dispersive surface energies and specific free energies.

Column	ΔG [kJ/Mol] (1-Hexanol)	ΔG [kJ/Mol] (Butyl acetate)	γ_d $[mJ/m^2]$	σ_d $[mJ/m^2]$	σ_{AB} $[mJ/m^2]$
Untreated	16.929	17.148	18.72	23.8	24.6
Bleached (60 min)	18.644	20.815	25.11	30.4	28.7
UV treated (74 h)	19.570	21.806	28.05	31.6	43.4

σ_d and σ_{AB} are the surface energy values for the dispersive and the polar contribution obtained from wettability measurements. The latter were carried out with diiodomethane, formamide and water. Although absolute numbers are rather different the trend in both measurements is the same. Both kinds of treated fibres show significantly higher values compared to the untreated material. Moreover UV treatment leads to higher numbers than chemical bleaching. These effects may be due to damage of the surface structure, which makes the surface more heterogeneous. These treatments can also cause an increase of the hair porosity.

Conclusion

Surface energies may be readily studied using an IGC SEA at infinite dilution. Moreover IGC SEA provides the possibility, as opposed to other techniques, to study surface energies at different concentrations, which can give a heterogeneity profile of the surface. In the particular case of these hair samples, this can provide a more detailed picture of the changes caused by different treatments. Additionally a study of porosity by both polar and non-polar vapours could complete the obtained picture.

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