iGC SEA
Application
Note 220

The Characterisation of Cotton Fabrics and the Interaction with Perfume Molecules by Inverse Gas Chromatography

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IGC SEA is a versatile tool in the characterisation of textile products and the interaction with perfume molecules due to the wide range of physicochemical parameters, which can be determined by this technique. This is demonstrated by means of cotton wool and cotton fabrics. Alkanes, fragrance molecules and other polar probes have been used to measure interaction parameters such as dispersive surface energy and specific free energy. Experiments at different relative humidities gave additional information about the impact of water adsorption on the measured properties.

Introduction

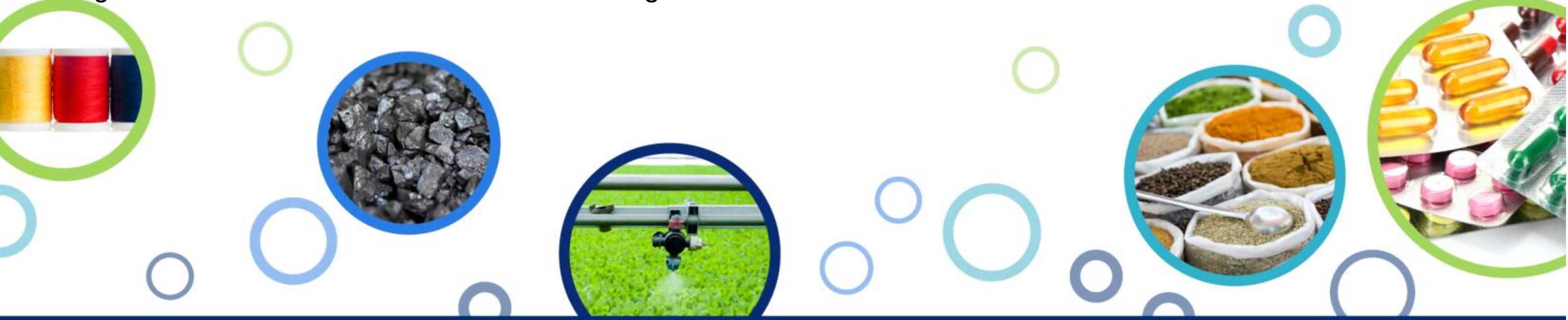
The use of physicochemical parameters is a common and useful way for the description of textile products and their interaction with fragrance molecules [1].

Inverse gas chromatography (IGC SEA) provides a fast and accurate utility for the determination of these parameters in any required concentration range. IGC SEA has advantages especially for measurements in the infinite dilution region compared to other techniques due to its high sensitivity. At these small concentrations only the highest energy sites of a heterogeneous solid surface interact with the vapour molecules. Therefore, all parameters obtained in this range show the highest sensitivity to differences between materials.
This can be applied to making distinctions between different products obtained from the treatment of the same starting material. Typical examples are bleaching or dyeing processes.
In the case of an experiment with polar probe molecules, acid-base interactions can be investigated. The obtained free energy values give a direct measure of the strength of interaction for different surface sites. Free energy values obtained from measurements with polar or non-polar flavour and fragrance molecules allow a description or even a prediction of important processes such as flavour/fragrance release or storage stability.

The application of IGC SEA is demonstrated in this paper using different experiments.
The first and second series of measurements were carried out on cotton fabrics. In these experiments the dispersive surface energy was determined as well as the free energy for several flavour and fragrance components. Additionally heat of sorption measurements were performed. To address the influence of humidity on the results these experiments were carried out at different relative background humidity levels.
The third set of experiments includes the determination of the dispersive surface energy as well as the free energy of a few acid-base probes for bleached and unbleached cotton wool.

Theory

Surface energy, free energy and heat of sorption parameters can be determined by pulse inverse



gas chromatography. In this experiment a small amount of an organic vapour is injected into a carrier gas stream. At infinite dilution the adsorption is independent of the surface coverage of the adsorbed molecules. The result is a linear adsorption isotherm, which can be described by Henry's Law. In this case the experimentally obtained peaks are symmetrical (Gaussian) and the retention time from the peak maximum can be used to calculate the retention volume. The net retention volumes V_N are computed using Equation 1.

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

where T is the column temperature, m 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.

In the Henry's Law region the net retention volume is related to the differential heat of sorption by Equation 2.

$$\ln V_N / T = -\Delta H_A / RT + C \qquad (2)$$

where it is assumed that the adsorption enthalpy is independent of temperature. Under these conditions the heat of sorption is obtained from a plot of $\ln V_N/T$ versus $1/T$ [1].

The relationship between the retention volume and the dispersive surface energy is given by Equation 3:

$$RT \ln V_R^0 = 2N_A \left(\gamma_S^D\right)^{1/2} a \left(\gamma_L^D\right)^{1/2} + const. \qquad (3),$$

where R is the gas constant and T the column temperature. a is the cross sectional area and γ_L^D is the surface tension of the probe molecule. By injecting a series of alkanes a linear graph is obtained from the plot of RTlnV versus $a_{*}\gamma_L^D$. The dispersive surface energy γ_S^D can be calculated from the slope. The theoretical background of this procedure is described in [2].

If polar probes are injected points will be located beyond the alkane straight line since polar probes show a dispersive and specific interaction. Thus, the distance between the straight line and each point of a polar probe molecule represents the specific free energy according to Equation 4:

$$\Delta G_{sp} = \Delta(RT \ln V_N) \qquad (4)$$

One alternative approach is the plot of RTlnV versus the logarithm of the partial pressure [3]. This method allows only the determination of ΔG_{sp}.

Method

Various columns (SMS standard column with 2mm ID and 30 cm length) were packed with either cotton wool or cotton fabrics. The cotton fabrics were cut in strips of 7.9 x 1.0 inch (~ 20 x 2.5 cm), rolled and pulled through the column by using a thin metal wire. The packing procedure is described in [4].

All sorption experiments were carried out on an SMS-*iGC* 2000. Measurements were undertaken with various non-polar and polar probe molecules, supplied by Aldrich. All surface energy experiments were carried out at 303 K at 10 ml/min carrier gas flow rate. The same flow rate was used for the heat of sorption measurements.

Before measurement a pre-treatment was carried out for 3 h at the measurement temperature, relative humidity (RH) and flow rate. Methane was used as a tracer and helium as the carrier gas.

Calculations were performed using the SMS-*iGC* Analysis Software v1.1 .

Results

The dispersive surface energy is obtained from a plot of RTlnV versus the cross sectional area times the square root of liquid tension. Since the latter parameters are usually not available for flavour and fragrance molecules this plot is not applicable for the calculation of free energy values. Therefore, a plot of RTlnV versus the logarithm of the saturation pressure is used to determine the specific free energy for the two polar probes, ethyl- and amyl acetate (see Figure 1).

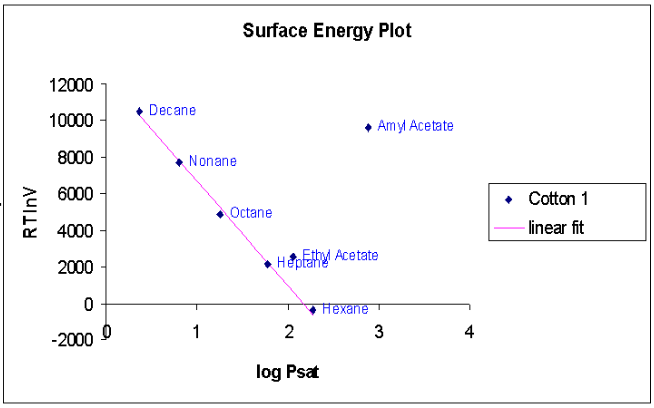


Figure 1. *RTlnV versus log p(sat.) - plot for cotton fabrics at 303 K and 10 ml/min carrier gas flow rate.*

Table 1 gives the obtained values for the dispersive surface energy and free energies for ethyl acetate and amyl acetate. Measurements were done twice on the same column packed with the cotton fabrics.

Table 1. Surface energy and free energy measurements on cotton fabrics.

Experiment	**Surf.Ener. (mJ/m2)**	**ΔG Ethyl acetate (kJ/Mol)**	**ΔG Amyl acetate (kJ/Mol)**
Run 1	41.05	1.995	13.754
Run 2	41.96	1.978	13.864

The values show a very good reproducibility (error <2%). The interaction of amyl acetate with the surface is much stronger than that of ethyl acetate.

For heat of sorption measurements on cotton fabrics octane, R-(+)-limonene and amyl acetate were used as probe molecules. Figure 2 shows the heat of sorption plot by means of limonene.

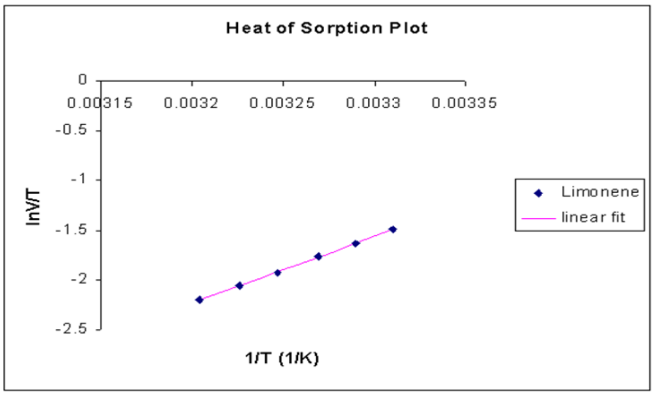


Figure 2. Heat of sorption plot for limonene on cotton fabrics between 302 and 312 K at 10 ml/min carrier gas flow rate.

The measurement with octane was carried out at two different partial pressures between 302 and 312 K to study the influence of the coverage dependence of the results which is directly related to the surface heterogeneity. In the infinite dilution region we obtained 49.91 kJ/Mol and at finite dilution 47.09 kJ/Mol. Considering the reproducibility error margin there is a small contribution from surface heterogeneity. The lower values at higher concentration make sense, as with increasing partial pressure increasing numbers of less active sites will be involved in the interaction with the probe molecule. A comparison with the literature [1] shows a good coincidence of the values here obtained with the reported value of 44.4 kJ/Mol, (measured between 308 and 333 K) considering the different origins and treatments of the cotton samples.

The heat of sorption at infinite dilution was also determined, using limonene and amyl acetate at different relative humidities. Limonene showed a values of 56.46 kJ/Mol at 0% RH and 54.25 kJ/Mol at 40% RH. Amyl acetate showed 56.54 kJ/Mol at 0% RH and 50.20 kJ/Mol at 40% RH. These differences are significant relative to the error margin. As expected the heat of sorption decreases with increasing RH. The interesting point is that the drop is much higher for the more polar and hydrophilic amyl acetate than for the less polar limonene. This can be explained by the fact that at 40% RH, water covers the highest polar energy sites. Limonene is interacting with less polar sites so the impact of the RH is less significant than for the amyl acetate.

The almost identical numbers for both probe molecules at 0% RH are considered as a coincidence.

Last but not least the influence of a surface treatment on the results was investigated. This was done by comparison of bleached and unbleached cotton wool. Table 2 shows a summary of the results.

Table 2. Surface energy and free energies for bleached and unbleached cotton wool.

Sample	Surf.Ener. (mJ/m2)	ΔG Ethanol (kJ/Mol)	ΔG Ethyl acetate (kJ/Mol)	ΔG Dioxane (kJ/Mol)
Unbleached	35.18	8.72	7.02	6.44
Bleached	45.27	11.54	9.22	9.46

The reproducibility was measured for column to column and experiment to experiment. Errors were in the usual margins (< 2 % for experiment to experiment and < 3 % for column to column).

Both the dispersive surface energy and the free energy of different polar probes show a significant difference between the bleached and unbleached cotton wool. As expected the bleached materials shows higher values. Bleaching causes an increase in the surface roughness. Therefore, more active sites are available for the interaction. It is interesting to note that acid-base probe molecules of different nature indicate a similar change for all surface sites.

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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