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The characterisation of cotton fabrics and the interaction with perfume molecules by inverse gas chromatography (IGC)

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IGC is a versatile tool in the characterisation of textile products and the interaction of these materials with fragrance 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 component of surface energy and specific free energy in different experimental conditions (relative humidity, concentration, cotton sample type).

1. Introduction

The use of physicochemical parameters is a useful way for the description of textile product and perfume properties [1].

Inverse gas chromatography (IGC) is a fast and accurate analytical technique for the determination of these parameters in any required concentration range. IGC 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 probe 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 specific free energy values give a direct measure of the strength of interaction for different surface sites. Other energy parameters obtained from measurements with polar or non-polar flavour and fragrance molecules allow a description and a prediction of important processes such as flavour/fragrance release or storage stability.

The application of IGC 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 specific 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 specific free energy of a few acid-base probes for bleached and unbleached cotton wool.

2. Theory

Surface energy, specific 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.

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

where T is the column temperature, F is the exit flow rate at 1 atm and 273.15 K, 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

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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 $1/T$ [2].

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

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

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 $RT \ln V$ 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 [3].

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 difference between the straight line and each point of a polar probe molecule represents the specific free energy of desorption according to Equation 4:

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

An alternative approach is the plot of $RT \ln V$ versus the logarithm of the partial pressure [4]. This method allows only the determination of ΔG_{sp}.

3. Experimental

Various columns (SMS standard column with 2 mm ID and 30 cm length) were packed with either cotton wool or cotton fabrics. The cotton fabrics were cut in strips of 20 × 2.5 cm, rolled and pulled through the column by using a thin metal wire whereas the cotton wool was pushed into the columns using a thick metal wire. The packing procedure is described in [5].

All sorption experiments were carried out on an SMS-*i*GC 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 starting the measurements, the columns were pre-treated in situ for 3 h at the same temperature, relative humidity (RH) and flow rate as in the subsequent experiment. Helium was used as the carrier gas and methane was used to determine the gas phase dead volume. Calculations were performed using the SMS-*i*GC Analysis Software v1.1.

TABLE I Surface energy and specific free energy results on cotton fabrics

Experiment	Surf. Ener. (mJ/m^2)	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

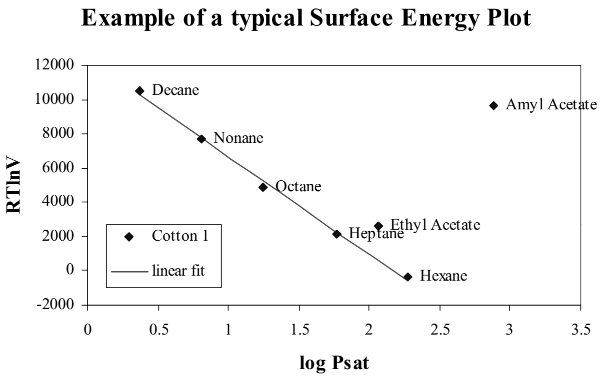

Figure 1 Plot of $RT \ln V$ versus log P (sat.)—cotton fabric, 303 K, 10 ml/min he flow rate.

4. Results

4.1. Determination of the dispersive component of the surface energy and the specific free energies of fragrance molecules on cotton fabrics

The dispersive surface energy is obtained from a plot of $RT \ln V$ 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 specific free energy values. Therefore, a plot of $RT \ln V$ 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 Fig. 1).

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

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 as can be seen form the difference in the free energy.

4.2. Determination of the heat of sorption of different molecules on cotton fabrics—investigation of the influence of concentration and relative humidity

Heat of sorption measurements have been carried out on cotton fabrics using octane, R-(+)-limonene and amyl acetate as probe molecules. Fig. 2 shows the heat of sorption plot by means of limonene.

The measurement with octane was carried out in a temperature range of 302–312 K. The experiment was run at two different concentrations (partial pressures) to study the influence of the coverage dependence of the results and therefore to get an insight into the surface heterogeneity.

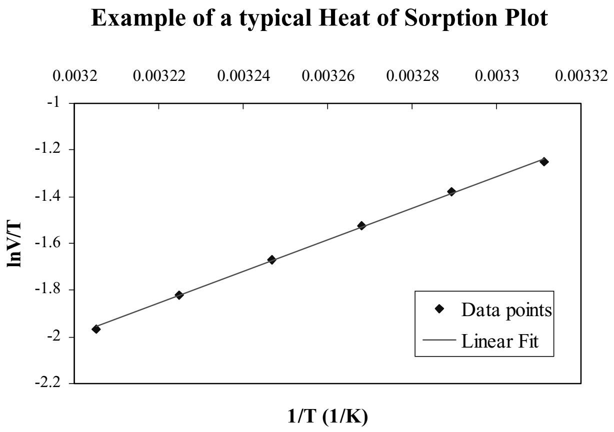

Figure 2 Heat of sorption plot for limonene ($P/P_0 = 0.5$) on cotton fabrics between 302 and 312 K at 10 ml/min carrier gas flow rate and 0% RH.

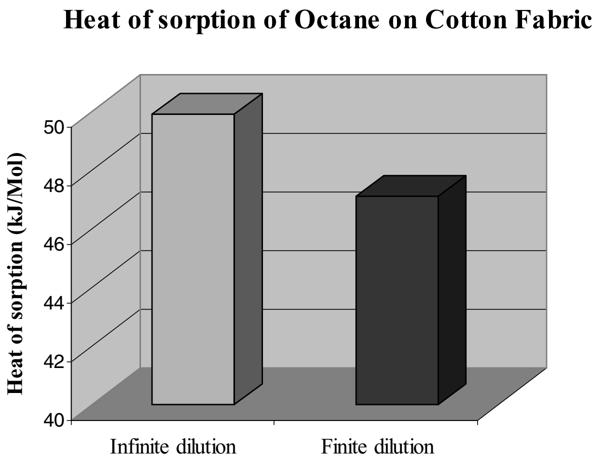

Figure 3 Heat of sorption of octane on cotton fabric as a function of concentration (temperature range: 302–312 K).

In the infinite dilution region (low concentration), we obtained a heat of sorption value of 49.91 kJ/Mol and at finite dilution (high concentration) 47.09 kJ/Mol. These results are illustrated in Fig. 3 and are in good agreement with the values obtained from literature [1] considering the different origins and treatments of the cotton samples (literature value: 44.4 kJ/Mol for a measurement between 308 and 333 K).

Considering the reproducibility error margin, the heat of sorption is significantly lower at finite dilution compared to infinite dilution. This is to be expected since with increasing partial pressures, an increasing numbers of less active sites will be involved in the interaction with the probe molecule.

This is an interesting phenomenon, which can be utilised in the determination of the surface heterogeneity of the sample.

The measurement of the heat of sorption of limonene and amyl acetate was carried out in a similar temperature range (302–312 K). The experiments were all run at infinite dilution but at two different relative humidities (0% and 40% RH) to study the influence of the presence of water molecules adsorbed on the surface of the cotton fabrics.

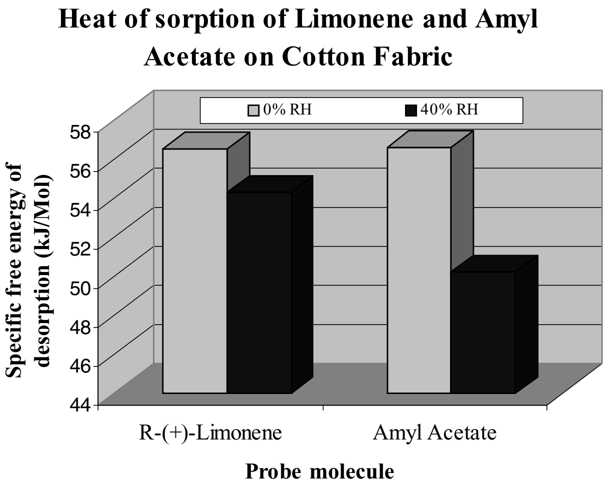

Figure 4 Heat of sorption for cotton fabric as a function of relative humidity (302–312 K/limonene & amyl acetate).

Limonene showed a value 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 results are illustrated in Fig. 4.

The differences observed between the results obtained at 0% RH and 40% RH for both, limonene and amyl acetate, are significant relative to the error margin. The heat of sorption decreases with increasing RH. This can be explained by the fact that at high relative humidity, some of the most active sites (which interact at 0% RH) are covered by water molecules. Therefore, with increasing relative humidity, less active sites will be involved in the interaction with the probe molecule and the heat of sorption decreases.

The difference in heat of sorption at 0% RH and 40% RH is significantly bigger for amyl acetate than for limonene. This can be explained by the fact that amyl acetate is more polar and hydrophilic than limonene and consequently is more likely to compete with water molecules for the same interaction sites. Therefore, the presence of water molecules at 40% RH has a much bigger impact on the amyl acetate adsorption.

In conclusion, with increasing partial pressure of octane or with increasing relative humidity in the case of limonene and amyl acetate, less active sites will be involved in the interaction with the probe molecule, and therefore the heat of sorption on cotton fabric is lowered.

4.3. Determination of the dispersive surface energy and the specific free energies on bleached and unbleached cotton wool—study of the influence of surface treatment

In this study, the influence of surface treatment on the dispersive surface energy and specific free energy of cotton wool has been investigated.

All results are summarised in Table II and illustrated in Figs 5 and 6.

The experiment-to-experiment and column-to-column reproducibilities were within the typical error margin (<3%).

TABLE II Surface energy and free energies for bleached and unbleached cotton wool

Sample	Surf. Ener. (mJ/m^2)	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

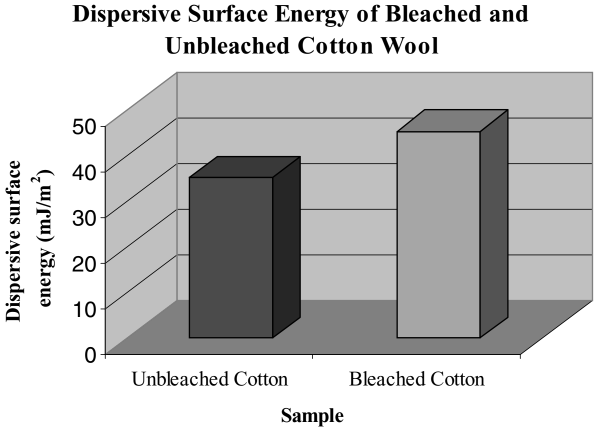

Figure 5 Dispersive component of the surface energy for bleached and unbleached cotton wool (303 K, 10 ml/min he, $P/P_0 = 0.03$).

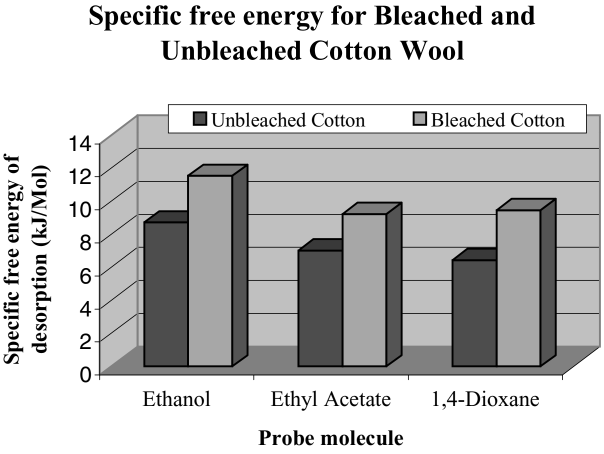

Figure 6 Specific free energy for bleached and unbleached cotton wool (303 K, 10 ml/min he, $P/P_0 = 0.03$).

The bleached cotton wool shows significantly higher values for the dispersive surface energy and the specific free energy of all polar probe molecules than the unbleached cotton wool. This was to be expected since 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.

5. Conclusions

IGC was demonstrated to be a fast and sensitive technique for the characterisation of cotton fibres and fabrics.

Bleached and unbleached cotton wool could be shown as significantly different in terms of surface energy and specific free energy for several probe molecules. Flavour and fragrance molecules with different polar character showed a difference in the adsorption behaviour on cotton fabrics under the influence of relative humidity.

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