iGC SEA Application Note 209

An investigation of Chromosorb silicas as support materials for Inverse Gas Chromatography

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Chromosorb materials are interesting candidates for the support of viscous liquids in inverse gas-solid and gas-liquid chromatography. The tests conducted in this study include the determination of the material surface energy and its specific interaction with a range of polar probes.

Introduction

Inverse gas chromatography (IGC SEA) was developed as a technique in the 1950's and 1960's for the physicochemical characterisation of solid materials. It does this by reversing the role of the stationary and mobile phases in what has become 'traditional' gas chromatography (GC). In this way the surface properties of a solid sample (the stationary phase) are probed by the elution of a well-defined solvent vapour or gas peak (the mobile phase).

IGC SEA studies are not only limited to rigid solid materials. There also is considerable interest in the determination of gas/vapour-liquid interactions. These kind of liquid samples are typically molten polymers [1], crude oil compounds [2] or other highly viscous materials. As it would be difficult to stabilise liquids in a vertical column the samples need to be supported on a solid carrier system, typically a homogenous powder with considerable surface *area* but low surface *energy*, to avoid strong interactions of the probe molecule with surface sites not covered by the liquid film.

In this study different kind of Chromosorb materials have been investigated since they were likely to be good candidates based on their surface area, inertness and chemical properties.

Method

The samples for the studies were kindly supplied by World Minerals (Celite Corporation). Both non-acid washed and acid washed samples of Chromosorb G, W and P and a sample of Celite Corp. Chromosorb 750 (all 60-80 mesh) were tested by packing approximately 150mg into a 2mm ID glass column. This was tapped using the SMS Column Packer until no further settling of the material occurred. The samples were then tested without further treatment other than to equilibrate for two hours at the set conditions. The same conditions were used for all samples (30^{o}C, 0% RH, 10ml/min He carrier flow). The samples were tested by measuring the elution time of a series of alkane injections (heptane, octane, nonane, decane and undecane) and polar probes (toluene, acetone, ethyl acetate and ethanol), all Sigma-Aldrich, HPLC grade. The injections were 250□l of solvent vapour at a concentration of 3%. Dead volumes for the instrument were measured using methane at a concentration of 15%. These injections allowed the calculation of the dispersive (non-polar) component of the surface energy and

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the specific polar interactions for the four polar probes used.

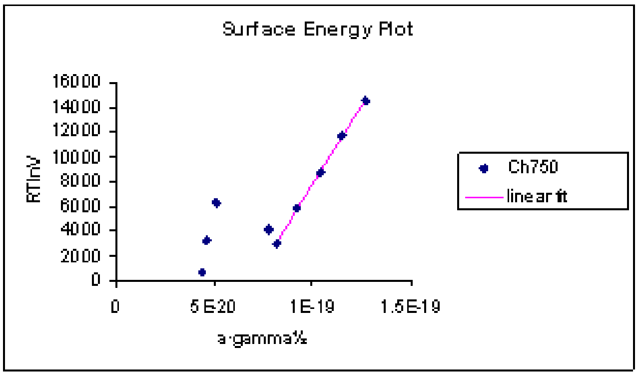

Figure 1. Dispersive surface energy and polar interaction plot for Chromosorb 750.

Dispersive surface energies were calculated according to the well-established method described by (amongst others) Schultz et al. [3,4]. This requires the natural logarithm of the retention volume to be plotted against the term $a(\gamma_L^D)^{1/2}$ for a series of alkanes, where 'a' is the cross sectional area of one adsorbed probe molecule and γ_L^D is the dispersive surface tension of the probe liquid. An example is given in Figure 1 for Chromosorb 750 and the dispersive surface energy is calculated from the slope of the straight line fit (heptane, octane, nonane, decane and undecane, left to right). All analyses were carried out using the SMS *iGC* Analysis Suite v1.1.

Polar interactions are calculated by plotting the retention volumes in the same way, and measuring the vertical displacement from the straight line fit caused by the specific (non-dispersive) interaction. These are also shown in Figure 1 for (left to right) ethyl acetate, acetone, ethanol and toluene.

Results

The results for all seven samples are summarised in Table 1.

Table1. NAW: Non acid-washed; AW: Acid-washed;

Sample	**Surface energy***	**Specific polar interactions (kJ/mol)**			
	(mJ/m^2)	Toluene	Acetone	Ethyl acetate	Ethanol
'G' NAW	50.8 (5)	6.1	19.4	19.1	-
'G' AW	45.3 (4)	5.9	21.6	-	-
'W' NAW	66.8 (4)	5.1	21.3	-	-
'W' AW	48.0 (5)	5.1	20.1	17.1	21.4
'P' NAW	80.1 (2)	7.6	-	-	-
'P' AW	61.4 (3)	7.0	13.0	11.5	18.2
'750'	44.4 (5)	2.0	7.2	9.1	10.9

** Number in parentheses gives number of alkane points in the fit.*

The four samples show a considerable range in energetic properties, but a pattern between the samples is evident. Sample 750 has the lowest dispersive surface energy, followed by Chromosorb G, Chromosorb W and Chromosorb P which has the highest dispersive surface energy. In each case, acid washing of the sample results in a significant lowering of the surface energy. Acid washing is carried out to remove trace impurities such as metals. These adsorption sites generally have high dispersive binding energies and so their removal is clearly seen by IGC SEA which is very sensitive to the highest energy binding sites. The surface energy is calculated from a straight line fit to the alkane elution times. For this study a cut-off time for data was imposed of 15 minutes. The number in parentheses alongside the surface energies in Table 1 shows the number of alkanes eluted within this cut-off. As can be seen, the highest surface energy materials only elute the smallest alkanes in this time.

The polar probes show a more complex trend in line with the specific nature of the interactions involved. Toluene, a hydrophobic probe, has the weakest interaction with all the materials, with Chromosorb 750 being the weakest followed by Chromosorb G, Chromosorb W and highest of all Chromosorb P. This is in a similar trend to the dispersive surface energies (Chromosorb G and W being the other way around). Acetone, a more hydrophilic probe, shows a similar trend to Toluene but with much higher interactions. Ethyl acetate and ethanol, both highly hydrophilic polar molecules interact very strongly, and in many cases did not elute within the 15 minute cut-off. Acid-washing of the materials had only marginal effects on the polar interaction energies suggesting that the impurities that have such a large effect on the dispersive energies, do not dominate polar adsorption. The two types of interaction may occur on different surface sites.

The requirements for a support are a material that allows for a spreading of the liquid on one hand but a moderate interaction with the vapour phase probe molecule on the other. For this reason the support material needs to be chosen based on individual requirements of the liquid-vapour system under investigation.

Conclusion

Seven samples of Chromosorb column packings were tested as possible support materials for Inverse Gas-Liquid Chromatography. Clear differences between the samples were observed, including the effects of acid washing and polar interactions.

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References

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