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iGC SEA Application Note 302

An Overview - Characterisation of Strong Solid-Vapour Interactions by iGC SEA

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Inverse Gas Chromatography (iGC SEA) is a very versatile technique for the characterisation of different types of material. This Application note focuses on the investigation of strong probe molecule – surface interactions and describes appropriate iGC SEA experiments for their investigation.

Introduction

The solid material is characterised by a vapour or gas (probe molecule, adsorptive) with known physico-chemical properties. Depending on the activity of the surface and the probe molecule adsorption can occur as physisorption or chemisorption.

Method

iGC SEA can generally be carried out as a discontinuous pulse or continuous frontal experiment. In the first case a peak is obtained while in the latter a frontal chromatogram can be observed. Experiments can be performed at finite or infinite dilution. Infinite dilution measurements take place in the Henry range of the isotherm and provide a high sensitivity due to the interaction of the probe molecules with the highest energy sites.

One of the most commonly measured parameters in this range is the surface energy. In this method a series of alkanes is injected to determine the dispersive component of the surface energy. It can be obtained from the slope of the straight line in a plot of RTlnV versus a*gamma1/2, where gamma is the surface tension of the liquid, a the cross sectional area and V the retention volume. Additionally, polar probe molecules can be injected and the difference of their position in this plot to the alkane straight line corresponds to the specific free energy for the interaction of the surface with the polar molecule. An example is shown in Figure 1.

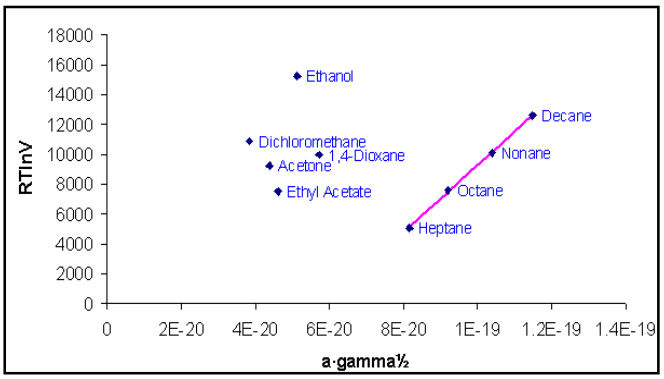

Figure 1. Typical plot for a surface energy experiment with four alkanes (dispersive interaction) and five polar probe molecules (specific interaction).

Results





Free energy values can also be converted into acid-base numbers by applying the Gutman or van Oss concept [1].

The benefits of the iGC SEA approach compared to wettability experiments are obvious: the higher sensitivity (wettability experiments see only average values for all sites), the wider variety of probe molecules and the ease of using powders. For these reasons iGC SEA surface energy experiments are a successful tool in the investigation of batch-to-batch problems, composite interactions and other, adhesion related problems. Examples can be found in [1] and [2].

In some cases it is also interesting to study the distribution of different energy sites over the surface rather than exclusively high energy sites. These sorts of experiments are carried out in the finite concentration range where the retention behaviour is measured at different concentrations. The retention volume is a direct measure for the heterogeneity of the surface and distribution functions can be derived. This is demonstrated by means of graphite in reference [3].

Both finite and infinite concentration experiments are based on the assumption of a physisorption interaction. For some probe molecule-surface interactions this assumption is not valid due to the strong nature of the adsorption process. These kinds of interactions can be divided into reversible and irreversible (chemisorption) interactions. In the latter case the probe molecule forms a strong bound with the surface and the process is irreversible, the classical case of a chemisorption. Chemisorption interactions can be investigated by titration methods. In a titration experiment, pulses with the same concentration are injected until the peaks have the same height [4]. The difference in the peak area represents the amount of irreversibly adsorbed vapour. This is the simplest case of a titration experiment. An example is shown in Figure 2.

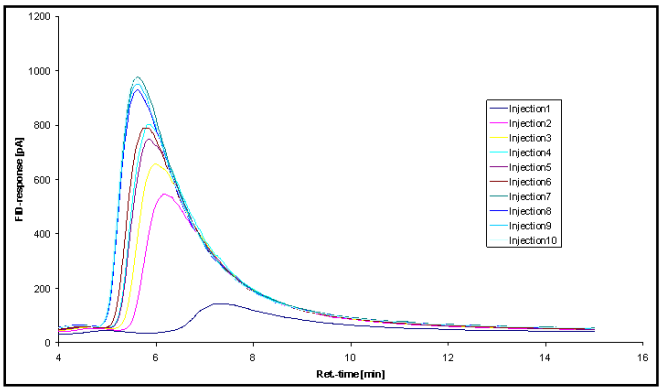

Figure 2. Titration experiment for the determination of the irreversibly adsorbed amount.

A more sophisticated study can be done by varying the concentration and the temperature. However, only the amount of irreversibly adsorbed molecules is considered. An extension of this method to reaction-iGC SEA is also possible. In this experiment the reaction is observed in-situ and a combination of FID with an analytical column (or better a mass spectrometer) is used to identify the products of the reaction.

In some cases interactions can be extremely strong but still reversible. This could cause a very slow, kinetically controlled desorption of the probe molecules from the surface. In order to overcome the activation barrier of desorption for these strongly but reversibly bounded species, the temperature can be increased in a ramping experiment. Such an experiment can be done by a thermal programmed desorption (TPD) or flash thermal desorption (FTD). The first method involves a slow ramping rate (typically 3K/min) and different highly energetic sites on the surface can be identified. An example is given in Figure 3. The FTD approach requires a fast ramping rate of ca. 50 K/min and allows targeting certain high energy sites. In reference [5] FTD was used to separate micropores from outer surface and mesopores.

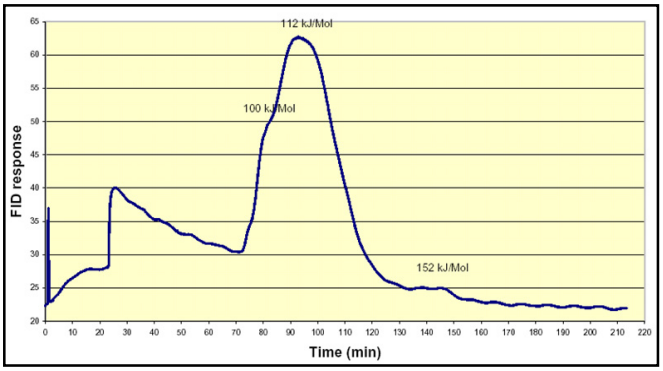

Figure 3. iGC SEA*/Thermodesorption with a ramping rate of 3 K/min (Butanol on Activated Carbon)*

In principle, both methods can be used for either micropore or surface group characterisation. The choice of probe molecules should allow distinguishing between both. Micropores should display the same effect for polar and non-polar probe molecules whereas specific groups on the surface shouldn‘t show any strong interaction with non-polar probe molecules.

Conclusion

iGC SEA is a very versatile and sensitive technique for the characterisation of various materials. All experiments mentioned above can be done with the same instrument. For thermal desorption and high temperature isothermal measurements a special high-temperature, fast ramping column heater is available. The experiments are easy to set-up, fully automated and fast, due to a unique sophisticated mass flow control system design.

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References

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