

# DETERMINATION OF THERMODYNAMIC PARAMETERS OF CARBON BLACK BY FRONTAL INVERSE GAS CHROMATOGRAPHY

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## **Introduction**

Carbon black is an often-applied filler in many industrial products. It is still one of the most important components in rubber reinforcement in today's tire and rubber industry, therefore, the characterization of its surface properties is of high importance in order to maintain and improve product quality.

Inverse gas chromatography (IGC) is a well-known tool for the characterization of carbon black [1].

In contrast to analytical chromatography, IGC represents the adsorption of a known adsorptive on an unknown adsorbent. The adsorbent (solid sample) is placed in the GC column, whilst the adsorptive can be a gas or vapor of the probe molecule. The retention behavior represents a direct measure for the interaction between the adsorptive and the sample. Therefore, the retention volume can be directly correlated with the physico-chemical parameters of interest [2].

Measurements of energetic parameters are carried out usually in the infinite dilution range. This range represents the linear part of the sorption isotherm (Henry region). In this region the uptake is independent of the surface coverage and interaction takes place only between the probe molecule and the highest energy sites. This fact leads to high sensitivity of parameters measured in the infinite dilution range. These parameters are typically heat of sorption, surface energy, and free enthalpy or entropy [3]. Since these measurements can be carried out with both non-polar and acid-base components, the obtained parameters can be used to characterize the surface chemistry and also to measure the magnitude of the interactions.

IGC methods can be divided into pulse and frontal measurements. Pulse methods are discontinuous and involve an injection of a certain amount of a vapor into the carrier gas stream. The adsorptive is transported by the carrier gas to the adsorbent in the column. In the ideal case

an equilibrium state is reached. The adsorbed substance will then be eluted by the following carrier gas and the detector of the GC can detect this elution as a peak. In a frontal experiment the probe molecule is continuously added to the carrier gas stream. Therefore, a breakthrough curve is obtained rather than a peak. The retention time of a pulse experiment can be obtained from the peak maximum or the center of mass, which should be very similar for an infinite dilution measurement since the peak is generally symmetrical in this region. For a frontal experiment, the retention time can be obtained from the turning point. In both cases the net retention volumes  $V_N$  are computed using Eq. 1.

$$V_N = jF / m \cdot (t_R - t_0) \frac{T}{273.15} \quad (Eq.1)$$

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,  $t_0$  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.

By varying the temperature in an IGC experiment, a change in the retention volume can be observed. This relationship can be used for the calculation of the heat of sorption. In the Henry’s Law region the net retention

volume is related to the differential heat of sorption  $\Delta H$  by Eq. 2.

$$\ln V_N = -\Delta H_A / RT + C \quad (Eq.2)$$

where it is assumed that the sorption enthalpy is independent of temperature. Under these conditions the heat of sorption is obtained from a plot of  $\ln V_N$  versus  $1/T$  [2].

Although pulse measurements have been used quite successfully they are limited to smaller surface area materials or higher measurement temperatures. This is due to the fact that peaks for small injections at infinite dilution are very small and broad and therefore difficult to analyze. This problem cannot always be solved satisfactorily by using higher temperatures since the heat of sorption is different or, in some cases, reaction between the adsorbent and the probe molecule even occurs.

An alternative is the use of frontal measurements. Such a continuous experiment can provide a well-defined breakthrough curve, even at small concentrations and low temperatures. The method was only applied in the past at finite dilution since an accurate setting and maintenance of a small vapor concentration is experimentally difficult to realize. With modern flow control technology, the frontal method can be used for the determination of thermodynamic parameters at infinite dilution. In the current paper heat of sorption measurements have been

carried out on carbon black to check the feasibility of the frontal method.

## Experimental

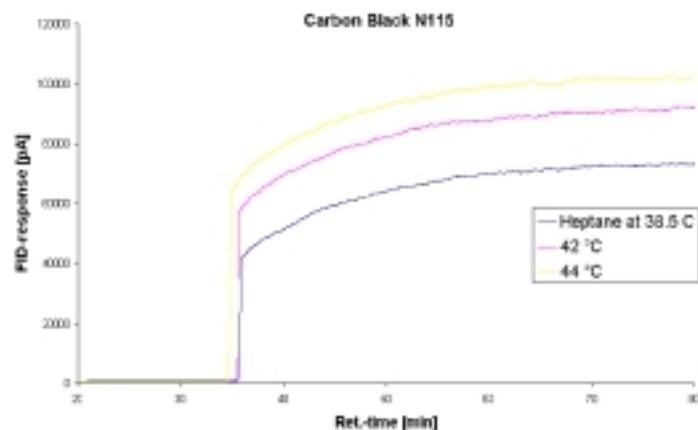
Carbon black N115 was supplied by Cabot, Boston, MA and heptane by Aldrich, UK.

The sample was packed into a silanized glass column (30 cm long, 2 mm ID) without prior solvent extraction. Prior measurement the sample was pre-treated at 403 K for 5 hours in situ.

All measurements were carried out using the SMS-IGC 2000 system. The sample was measured between 311 and 315 K and between 385 and 397 K in both pulse and frontal mode with a carrier gas flow rate of 15 ml/min. Heptane was injected in a concentration of 0.03 p/po via a loop with 0.25 ml volume. The obtained peaks showed a symmetrical shape, which confirmed infinite dilution conditions. The dead time was determined by a methane injection.

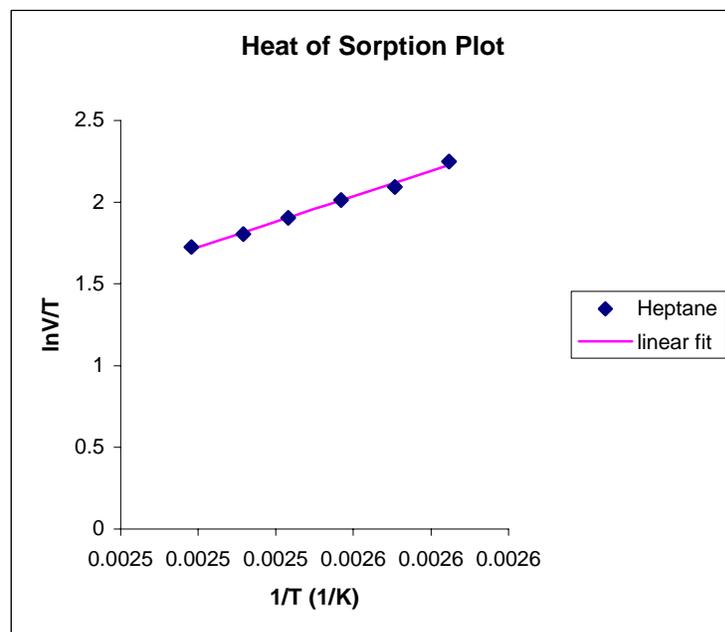
## Results and Discussion

Fig. 1 shows a set of adsorption breakthrough curves measured between 311 and 315 K.



**Figure 1.** Breakthrough curves for heptane on carbon black N115. Measurements were carried out at infinite dilution in a pulse experiment between 311 and 315 K.

Fig. 2 shows a typical heat of sorption plot by means of a heptane measurement on Carbon N115.



**Figure 2.** Heat of sorption plot of heptane on carbon black N115. Measurements were carried out at infinite dilution in a pulse experiment between 385 and 397 K.

The result for the pulse experiment at high temperatures was 64.58 kJ/Mol. At low temperatures no peak could be identified as expected due to the widening of the pulse. For the frontal experiment the heat of sorption was 70.29 kJ/Mol in the low temperature range, whereas at high temperatures no reliable measurement could be obtained. This was initially surprising since the frontal method was even supposed to deliver more accurate results due to the continuous equilibrium conditions. However, it appears to be rather a technical problem at the moment since the accurate determination of the turning point is more difficult than for the peak maximum. This doesn't affect the accuracy of the low temperature experiment due to the long retention times and the big differences in the retention volumes. For shorter retention times, however, the inaccuracy becomes more significant and the method less reliable. This problem can be solved by improving the raw data analysis. Therefore, a comparison of the pulse and frontal value should be put off until more accurate data are available.

A comparison with literature data is difficult since no values are published for N115. Therefore, we compared the results with literature data measured on N110, which should have similar energetic properties. Wang and Wolff

[1] provide a value of 78.8 kJ/Mol, measured in a temperature range between 423 and 483 K. This value is much higher than the numbers measured here considering the fact that even N220 has a value 74.4 kJ/Mol. These differences can be due to the differences in the pre-treatment. Firstly, no solvent extraction has been carried out in this study and secondly, a less drastic conditioning temperature has been applied here.

However, the values are in a similar range as literature values. More materials with well-known surface properties must be investigated to confirm the capability of the frontal method at infinite dilution.

## Conclusions

Frontal IGC at infinite dilution was introduced as a method for the measurement of energetic surface properties on carbon and other porous materials. It provides benefits compared to the usual pulse IGC experiment in the characterisation of porous materials with a considerable high surface area at low temperatures.

## References

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