

# DETERMINATION OF DEPENDENCIES BETWEEN THE NET RETENTION VOLUMES AND PARAMETERS CHARACTERIZING THE ADSORBENT PROPERTIES

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## Introduction

Gas chromatography is known and widely used first of all as an analytical method. Applying chemical compounds with well defined physical properties as the chromatographed substances (adsorbates), also enables to use the research technique for investigation the properties of carbon and non-carbon adsorbents [1]. In this case it is known as inverse gas chromatography. The application of gas chromatography for the investigation of adsorbents is still too little in comparison with its application in analysis. Depending on the conditions of carrying out of chromatographic process in this case we most often deal with non-ideal, linear chromatography [2] and more rarely with ideal, non-linear chromatography [3,4]. Only in a few papers describing adsorbent investigations one may find mentions about the obtained results at the conditions typical of non-ideal, non-linear chromatographic process [5].

During chromatographic measurements of adsorption process proceeding at dynamic conditions an equilibrium state is not always attained as in the case of static tests. Hence, there are still some doubts, if the results obtained on the basis of chromatographic measurements are plausible. The observed differences in the adsorption values are connected with the so-called molecular sieve effect connected with the similarity of the dimensions of the adsorbate molecules and the entrances to the micropores not being filled with the adsorbate in the chromatographic process. It leads to the question if the adsorption chromatographic tests can replace the static ones.

In this paper I have made an attempt of applying inverse gas chromatography for the evaluation of changes in adsorption pore space in virgin active carbons and loaded with the known amount of *tert*-butylbenzene and next regenerated by supercritical methods with CO<sub>2</sub>. The supercritical regeneration was carried out by two methods: dynamic and maceration. The active carbons of different sizes of grains in comparison with internal diameter of chromatographic column were tested.

## Experimental

### *Adsorbents and adsorbates*

The R commercial active carbon (Gryf-Skand, Hajnówka, Poland) and WS4 (Calgon Corp., USA) were used in the study. The mineral matter was removed from the part of the R adsorbent. Hereafter, this adsorbent was denoted as O. The grains of active carbons R and O had an average diameter of 0.30÷1.25 mm. The grains of the WS4 active carbon were cylinders 7 mm in length and 3.8 mm in diameter. The adsorbents were degassed in a vacuum drier at 453 K and 1.5÷2.5 kNm<sup>-2</sup> for 10 hours.

The mixture of methane and propane was used in the tests. The sizes of the samples injected onto the column were in the range 0.16÷1.17 cm<sup>3</sup>.

### *Static measurements*

The basic characteristics of the tested active carbons have been calculated on the basis of the nitrogen isotherms determined volumetrically at 77 K. The specific surface area calculated from these isotherms,  $S_{BET}$ , for the R, O and WS4 are 990, 1840 and 1290 m<sup>2</sup>/g, respectively and volumes of micropores 0.43, 0.61 and 0.51 cm<sup>3</sup>/g, respectively.

### *Chromatographic measurements*

The chromatographic measurements were carried out by means of a Unicam type 610 gas chromatograph with an on-line Unicam 4880 Chromatography Data Handling System which was started when injecting a sample. The R and O active carbons were placed in glass columns 65cm×0.2cm I.D., whereas the WS4 grains were placed in 65cm×0.4cm ones. The length of the adsorbent bed in each column was 6÷7cm. The part of the column unoccupied by the adsorbent was filled with glass beads of 80 mesh size. The filled column was mounted into the chromatograph thermostat and heated for 10 h at 603 K in a stream of helium with a flow rate of 40 cm<sup>3</sup>/min. The stream did not flow through the detector. The measurements of retention times of propane were carried out at 303 K for the R and O adsorbents, and at 308 K for the WS4 one.

## Results and Discussion

In the case of the R and O active carbons, for all the tested systems, the obtained chromatographic peaks were asymmetrical and their retention times depended on the injected sample size and the diffusive sides superimposed. For all the adsorption systems with the coarse-grained adsorbents the obtained peaks were also asymmetrical and their retention times depended on the injected sample size but the self-sharpening and diffusive sides did not superimpose. Taking into account the sets of peak profiles obtained I was in the range of linear and non-ideal chromatography for the R and O adsorbents, and in the range of non-linear and non-ideal chromatography for the WS4 adsorbent [6]. For the same volume of the injected adsorbate the retention times were reproducible in both cases.

Similar results were obtained by Flour and Papirer by adsorbing tetrahydrofuran on short glass fibers with a specific surface area  $0.30 \text{ m}^2/\text{g}$  [7]. Guichon and co-workers have studied such peak profiles in non-linear gas chromatography [5].

The dependencies between the pore volume filled with propane during the chromatographic process,  $W$ , and molar differential work of adsorption,  $A$ , were determined on the basis of chromatographically determined adsorption isotherms of propane at 303 and 308 K. The  $W=f(A)$  expressions were differentiated with respect to the molar differential work of adsorption. The obtained asymmetrical distribution functions of pore volume with respect to the molar differential work of adsorption had the extremums the co-ordinates of which depended on the amount of propane injected onto column, similar to the maxima of the propane peaks. For every tested adsorption system the obtained distributions functions were spreaded with increasing values of molar differential work of adsorption. It suggested that the distributions functions are approximated to the real distribution of propane adsorption energy on the tested active carbon surface, and the asymmetrical chromatographic peak, which the adsorption isotherm of propane was previously calculated from.

## Conclusions

The interdependence between the retention time of propane peak maxima and its profile and the extremum of distribution function of pore volume with respect to molar differential work of adsorption does exist.

In case of ideal, non-linear chromatography the profiles of the distribution function with respect to molar differential work of adsorption superimpose, like the profiles of diffusive sites of peaks.

On the basis of the mentioned distribution functions it is not possible to recognize if the

chromatographic process is ideal and non-linear or non-ideal and non-linear.

In the case of coarse-grained adsorbents, the pore volume filled with propane during the chromatographic process is significantly low in comparison to the fine-grained ones.

The adsorption isotherms of propane calculated by peak maxima method are the equilibrium partition isotherm of adsorbate between solid phase (adsorbent surface) and mobile phase (carrier gas) in the case of non-ideal, non-linear chromatography.

The regeneration of active carbons by means of supercritical  $\text{CO}_2$  is more effective in the case of dynamic method in comparison with the maceration one.

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## References

- 1 T. Paryjczak, *Gas Chromatography in Adsorption and Catalysis*, Polish Scientific Publishers, Warszawa, Ellis Horwood Limited, Chichester, 1986.
2. P.J.M. Carrott, K.S.W. Sing, *J. Chromatogr.*, 1989; 406:139-145.
3. M. Pyda, G. Guiochon, *Langmuir*, 1997; 13: 1020-1025.
4. B.J. Stanley, G. Guiochon, *Langmuir*, 1995; 11: 1735-1743.
5. A. Jaulmes, C. Vidal-Madjar, A. Ladurelli, G. Guichon, *J. Phys. Chem.*, 1984; 88: 5379-5385.
6. G. Edel, B. Chabert, *C.R. Acad. Sci. Paris*, 1969; ser.C 268: 226-231.
7. C.S. Flour, E. Papirer, *Ind. Eng. Chem. Prod. Res. Dev.*, 1982; 21: 666-672.