

NEW METHOD OF CALCULATION OF KOVÁTS RETENTION INDICES FOR SUBSTANCES CHROMATOGRAPHED ON CARBON ADSORBENTS

H. Grajek, Z. Witkiewicz, H. Jankowska, A. Świątkowski
Military Technical Academy, Institute of Chemistry, 00-908 Warsaw, Poland

Introduction

Inverse gas chromatography (IGC) is widely used for the investigation of both carbon and non-carbon adsorbents characterizing by a weakly and strongly developed micropore structure [1,2] and polymers [3]. From the chromatographic data the physico-chemical parameters of adsorption e.g., standard free energy of adsorption, surface energy and entropy of specific interactions are calculated. The suitability of IGC for physico-chemical investigations follows from the fact, that a chromatographic process is related to the properties and physico-chemical interactions of column filling (e.g. carbon or non-carbon adsorbent) with the chromatographed substances. Reflection of these interactions is the retention of chromatographed substances.

One of more important parameter characterizing a substance retention in precisely defined chromatographic system is Kováts retention index.

According to carrying out the chromatographic process in this case we most often deal with non-ideal, linear chromatography [4] and rarely with ideal, linear chromatography [5], and ideal, non-linear one [6]. Only in a few articles describing adsorbent investigations one may find mentions about the obtained results at the conditions typical of non-ideal, non-linear chromatographic process [7].

If retention time of adsorbate depends on amount of the adsorbate injected on column, then the retention volume and Kováts retention index also depend on it.

In this paper a new method for calculation of net retention volumes and Kováts retention indices calculated on the basis of them is described. The proposed method may be applied in the case when the temperature retention dependency is a continuous function in temperature interval in which the measurements are carried out.

Experimental

Adsorbents and adsorbates

The following activated carbons were used in the study: R i NP5 (Gryf-Skand, Hajnówka, Poland). The mineral matter was not removed from these adsorbents. The grains of active carbons had an average diameter of 0.30÷1.25 mm. The adsorbents

were degassed in a vacuum drier at 453 K and 1.5÷2.5 kNm⁻² for 10 hours.

The following substances: *n*-pentane (MERCK, ref. for gas chrom.), *n*-heksane (J.T. Baker, p.a.) and *n*-heptane (MERCK, ref. for gas chrom.), benzene (S.A. UCB, p.a.) and its reduction products cyclohexane (J.T. Baker, p.a.), cyclohexene (Fluka, p.a.) and 1,3-cyclohexadiene (Fluka, p.a.) were used as adsorbates. The sizes of the samples injected onto the column were in the range 0.005÷0.05 µl (3.5÷45 µg).

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 and NP5 are 990 and 1360 m²/g, respectively and volumes of micropores 0.41 and 0.53 cm³/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 active carbons were placed in glass columns 65cm×0.4cm I.D.. 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 cm³/min. The stream did not flow through the detector. The measurements of the retention times of the tested hydrocarbons were carried out over the temperature range 523÷593 K (except for cyclohexane on carbon NP5; 523÷553 K) in helium as the carrier gas at a flow-rate of 40±1 cm³/min by means of flame ionization detector, and gases by means of the thermal conductivity one.

Results and discussion

For all the tested systems, the obtained chromatographic peaks were asymmetrical and their retention times depended on the injected sample size and the self-sharpening and diffusive sides did not

superimpose. Taking into account the obtained peak profiles we were in the range of non-linear and non-ideal chromatography [1,2]. For the same volume of the injected adsorbate the retention times were reproducible.

Similar results were obtained by Flour and Papirer by adsorbing tetrahydrofuran on short glass fibers with a specific surface area $0.30 \text{ m}^2/\text{g}$ [8]. Guichon and co-workers have studied such peak profiles in non-linear gas chromatography [7].

The net retention volumes referred to 273.2 K and the specific surface area, $V_{S(273)}(m)$, calculated from the peak maximum retention times depended on sample size injected onto column, m . The net retention volume of the adsorbates increased to definite the value of the net retention volume at zero concentration of adsorbate [zero coverage of surface adsorbent with adsorbate, $V_{S(273)}^0(m)$] as the sample size decreased

In this case the net retention volume, $V_{S(273)}^0(m)$, is the physicochemical constant.

The net retention volumes at zero coverages calculated from the peak maximum retention times in the proposed method are connected with the same isotherm of partition and the same isotherm of adsorption of the chromatographed adsorbates at the interfaces [9].

Kováts retention indices have been calculated on the basis of the obtained values of the net retention volumes by two methods.

The first of them consisted in substituting the $V_{S(273)}^0(m)$ values to the classical equation. The other, new method consisted in describing the net retention volumes by the Antoine-type hyperbolic dependency in the column temperature interval of which they were determined. Next, the average values of the net retention volumes were calculated on the basis of the best fitting curve. The best fitting curve was computed by Levenberg-Marquardt method [10].

Analyzing the obtained results one may arrange the used adsorbates according to the increasing values of Kováts retention indices as follows:

on the R active carbon:

cyklohexene<1,3-cyklohexadiene<benzene
<cyklohexane in whole interval of the used temperature columns,

on the NP5 active carbon:

cyklohexene<cyklohexane<1,3-cyklohexadiene<benzene
– $523 \div 533 \text{ K}$
cyklohexane<cyklohexene<1,3-cyklohexadiene
<benzene – $543 \div 553 \text{ K}$
cyklohexene<benzene<1,3-cyklohexadiene – $563 \div 583 \text{ K}$
cyklohexene<1,3-cyklohexadiene<benzene – $573 \div 583 \text{ K}$

The arranging of the adsorbates according to the increasing values of Kováts retention indices are not much different from their sequence obtained on the basis of the classical calculation method of them:

on the R active carbon:

cyklohexene<1,3-cyklohexadiene<benzene
<cyklohexane – $523 \div 583 \text{ K}$
cyklohexene<benzene<1,3-cyklohexadiene
<cyklohexane – 593 K

on the NP5 active carbon:

cyklohexene<cyklohexane<1,3-cyklohexadiene<benzene
– $523 \div 533 \text{ K}$
cyklohexane<cyklohexene<1,3-cyklohexadiene<benzene
– $543 \div 553 \text{ K}$
cyklohexene<benzene<1,3-cyklohexadiene – 563 K
cyklohexene<1,3-cyklohexadiene<benzene – $573 \div 583 \text{ K}$
K
cyklohexene<benzene<1,3-cyklohexadiene – 593 K .

Conclusions

The proposed method of Kováts retention indices calculation:

- allows to avoid their big errors caused by errors in the determination of retention time;
- allows to obtain the results independent of the adsorbate amount injected onto the column;
- is useful for working out of the chromatographic data measured on non-ground microporous active carbons at relatively high carrier-gas flow rates.

The temperature dependency of Kováts retention indices may be described by a quadratic equation.

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