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PHYSICAL CHEMISTRY OF SEPARATION PROCESSES: CHROMATOGRAPHY

Nonlinear Gas Chromatography as a Way of Studying Inhomogeneous Sorbents

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Abstract—A way of organizing and processing the results from gas–chromatographic experiments to obtain chromatographic retention characteristics for a fixed concentration of sorbate in the gas phase or on the surface of the sorbent is proposed and substantiated. The suitability and expediency of such retention characteristics for describing the sorption properties of inhomogenous sorbents is demonstrated using a wide variety of adsorbents of different natures (activated carbons, swelling and nonswelling polymers, silicas and their silver derivatives) as examples.

Keywords: gas chromatography, adsorbents, surface heterogeneity, isosteric retention characteristics

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INTRODUCTION

The possibilities of gas chromatography as a physicochemical means of study are restricted by most real sorbents being the carriers of chemically, geometrically, and thus energetically inhomogeneous sorption fields. In the case of industrial aromatic copolymer Polisorb-1, residual multiple bonds, products of their oxidation, and possible impurities of catalysts manifest themselves in sorption processes [1]. The surfaces of activated carbons, which are most often used for the purification of gas and liquid flows, contain various oxygen-containing functional groups along with the basis face of graphite [2].

Industrial silica contains impurities of aluminum, iron, calcium, and sodium, and it was shown in [3] that even one-tenth of one percent of these impurities drastically alters the properties of an adsorbent. Defects in the structure of an adsorbent, thin pores, areas of globule contact, and inclusions of crystallites also generate centers of increased sorption potential on a surface. Even with chemically pure pyrolytic silochromes, isolated and conjugated hydroxyl groups and siloxane bridges are initially nonequivalent [4]. From the viewpoints of chemistry and geometry, composite materials are intrinsically inhomogeneous.

It is well known from chromatographic experience that low-molecular substances, which are responsible for the nature of sorption centers, produce diffused asymmetric elution curves on heterogeneous sorbents, the forms of which change with the injection volume.

The approaches to organizing chromatographic experiments and treating experimental data proposed in this work ensure retention characteristics related to the final injection volumes. In developing them, the authors considered sorption to be a quasichemical reversible equilibrium reaction of the formation of a sorption complex by molecules of low-molecular substance and sorption centers on an adsorbent's surface. One mechanism of molecular interaction or another proceeds on a heterogeneous surface, depending on the nature of a sorbate's molecules and their areas of localization on the sorbent's surface [5].

The degree of filling of a sorbent's surface by a sorbate changes along with the volume of a sample injected into a chromatographic column; i.e., the statistical combination of sorption centers that participate in the adsorption process changes. In other words, the combination of contributions from different types of sorbate–sorbent interaction and the form of the elution curve change. An asymmetric elution curve for each specimen can be considered the additive sum of a particular statistical combination of symmetric elution curves corresponding to each type of sorption center and sorption mechanism [6]. This approach was used in [7, 8], when multifunctional polymer phases for chromatography and ionic exchange were modeled by mixing monofunctional phases.

The maximum of the peak corresponding to the maximum concentration of sorbate vapor in the gas phase and making the largest statistical contribution was taken as the point on the resulting curve that was the statistical average and determined the retention time of substance for a given sample volume. The center of masses was used in the more correct approach in [9].

The inhomogeneity of a sorption field even in the range of equilibrium thus results in diffusion and the asymmetry of elution curve and the dependence of the position of its maximum or the center of masses, according to which such chromatographic retention characteristics as retention time τ and retention volume V are calculated.

In practice, the value of V in these cases is extended to zero sample and zero consumption of the carrier gas; or a reference substance referred to as a molecular probe, which is indifferent to the nature of sorbent as much as possible, is chosen [10]. However, the values of retention characteristics extended to zero filling are associated only with active, possibly random sorption centers, while an indifferent molecular probe does not distinguish between centers of various natures. The retention characteristics of the final sample volumes of a molecular probe responsible for the nature of a sorbent's surface are thus in line with the nature of the sorption field.

In this work, we present the results from chromatographic studies using the proposed procedures for a number of materials: PVTMS, poly(vinyl trimethylsilane), a material for selective membranes; Kh-60 and Kh-550, chitosans that are polysaccharides with molecular masses of 60 and 550 kDa, respectively; CTS-PAA, a polyelectrolyte complex of chitosan and poly(acrylic acid); PAM, a sulfonate-containing copolymer of aromatic polyamides; Psb-1 or Polisorb-1, a homogeneous wide-pore copolymer of styrene with divinylbenzene; Psb-Ag, Polisorb-1 modified with silver nanoparticles (the weight content of silver is 3%); AC, activated coconut coal for the purification of drinking water; AC-Ag, silver-containing activated carbon AC (Bar'er); C-120, industrial homogeneous wide-pore pyrolytic silica (silochrome); composites based on silochrome C-120 modified with silver nanoparticles (the weight fraction of metal is indicated in the designation of each specimen: C-120-1,3, C-120-8,2, and C-120-3,2(3 nm) and C-120-3,2(17 nm) composites containing silver nanoparticles with mean diameters of 3 and 17 nm, respectively); and C-120-Al_2O_3-Ag^+, silochrome C-120 with alumosilicate complexes grafted onto its surface and silver deposited via ionic exchange.

Several substances that are capable of different types of molecular interactions were used as references in studying each adsorbent.

Organizing a Chromatographic Experiment and Calculating the Retention Characteristics of Sorbates at a Fixed Concentration in the Gas Phase

Retention volume V_h of reference substances, calculated from retention time τ_h for peaks with equivalent height h that corresponds to identical concentrations in the gas phase, is in this case used to describe the sorption properties of materials. Since the retention volume characterizes the distribution of a substance between the gas and sorption phases, it is entirely determined by the concentration of sorbate in the sorption phase; i.e., only bythe nature of the sorbent—sorbate system at identical concentrations in the gas phase. The peak height corresponding to 100—500 mm at the lowest possible upscale of the signal in the linear range of potentiometer response is considered standard. If it is impossible to introduce the sample volume that yields a peak with the specified height, τ_h is calculated from elution curves recorded in a narrow range of sample volumes, assuming that dependence h—τ_h is linear in this range.

Organizing an experiment in this manner, the temperatures of structural transitions of PVTMS were determined for the first time via gas chromatography, using water as a molecular probe [11]. In the temperature dependence of $V_h(t)$ for water, deviations from monotonicity were observed at 60, 120, and 170°C, which correspond to relaxation processes associated with the intensified mobility of trimethylsilyl groups, relaxation related to the vibrational motion of short chains of macromolecular chain with branching, and the glass-transition temperature of PVTMS, respectively. These results were fully supported by calorimetry [12].

In [13, 14], sorption properties were described and the temperature of structural transitions of aromatic polyamide PAM and polyelectrolyte complex CTS-PAM was determined using this technique. Depending on $\ln V_h(1/T)$ of alcohols, a so-called Z-kink was detected (Fig. 1), indicating the transition of the polymer from a vitreous to a highly elastic state and the associated change in the mechanism of interaction, from physical adsorption to absorption [10].

Isosteric (i.e., those related to a particular concentration of sorbate on a sorbent's surface), chromatographic, and thermodynamic characteristics of sorption are more correct.

Organizing a Chromatographic Experiment and Calculating Isosteric Chromatographic Retention Characteristics

Elution curves in the possible range of sample volumes are recorded for each sorbate, reduced to a particular degree of the detector's signal upscale, and generate a spectrum from them (Fig. 2). The smooth l_h curve is then drawn through the peak maxima that represent the distribution of the maximum peak height—retention time corresponding to this maximum, $h_m - \tau_m$. At each point on this curve, concentration a of the sorbate in the sorbent, corresponding vapor pressure p in the gas phase, and isosteric retention volume V_{is} are calculated using the equations $a = bS_a/Mg$; $p = buh_mRT/Mw$; and $V_{is} = \tau_m wg$, where S_a is the area on the chart strip between the moment of the output of nonsorbed gas and the part of curve l_h up to

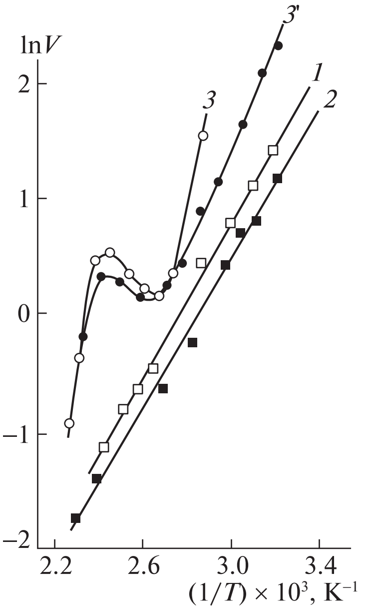

Fig. 1. Dependences of ln $V(1/T)$ for (*1*, *2*) *n*-octane and (*3*, *3'*) *n*-butanol for (*1*, *3*) initial and (*2*, *3'*) annealed PAM.

that point; b is the detector's response for sorbate at velocity u of the chart strip (this parameter is obtained via direct calibration); M is the molar mass of the sorbate; g is the mass of the sorbent in the column; R is the universal gas constant; T is the temperature of the experiment; and w is the consumption of carrier gas, reduced to experimental conditions [15]. Using basic sorption characteristics a, p, and V_{is}, we can calculate sorption isotherms and isosteres, isosteric thermodynamic characteristics of the process, the dependence of the isosteric retention volume on the degree of filling of the sorbent surface by sorbate $V_{\mathrm{is}}(a)$, and so on.

A necessary condition for valid results is to determine them in the equilibrium range of the process, where retention characteristics do not depend on the consumption of the carrier gas and this range of w values has been determined empirically for each system. With silica, carbons, and silver-containing composites, this range is 20–60 cm^3/min; for swelling polymers, it was 3–6 cm^3/min, due to the material's strong resistance to diffusion.

The sense of using isosteric retention values to describe the properties of sorbent was demonstrated in [16, 17]: for a molecular probe to induce structural transitions in a sorbent, the concentration of sorbate on a surface must be finite and sufficient. As an example, the Z-transition in the dependence of $\ln V(1/T)$ for 1-butanol on PAM was observed only for alcohol concentrations of $a > 2$ µmol/g, while the described structural transitions in PVTMS are induced by water concentrations of $a \geq 5$ µmol/g.

Dependence $V_{\mathrm{is}}(a)$, analysis of which allows quantitative and qualitative estimates of the inhomogeneity of a sorption field and a clear picture of the degree of sorbent filling by a sorbate and their mechanisms of interaction, is most informative. The nature of the sorbent–sorbate system and the experimental conditions determine the shape of curve $V_{\mathrm{is}}(a)$. Typical curves are shown in Fig. 3.

The shape of dependence $V_{\mathrm{is}}(a)$ of type 1 corresponds to the scenario of the adsorption of sorbate molecules on the most active sorption centers, which corresponds to the highest values of V_{is}. It should be noted that the high values of V_{is} in the range of low filling could also be due to the most favorable orientation of sorbate molecules with respect to the surface. With an increase in concentration a of sorbate on the sor-

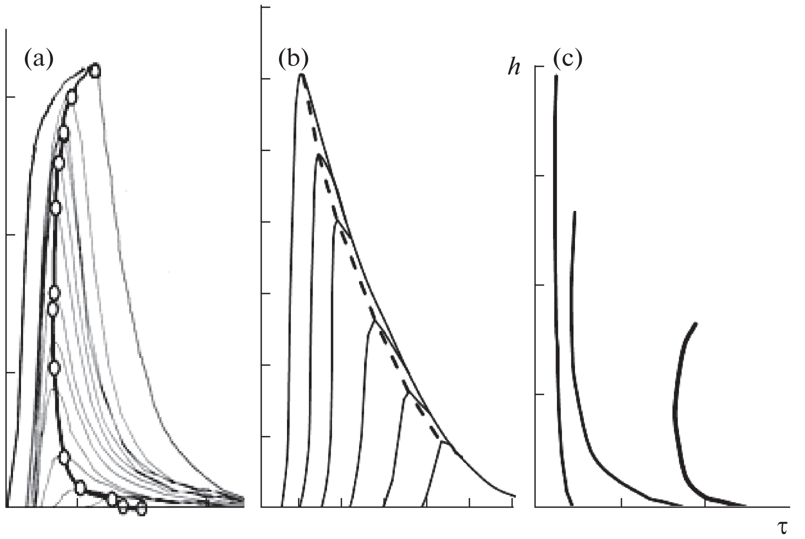

Fig. 2. Spectra of eluate curves: (a) ethanol on chitosan Kh-550 at 120°C, (b) water on silver-containing alumosilicate C-120-Al–Ag$^+$ at 200°C, (c) possible form of distribution curves $l_{\mathrm{m}} \sim h_{\max} - \tau_{\max}$.

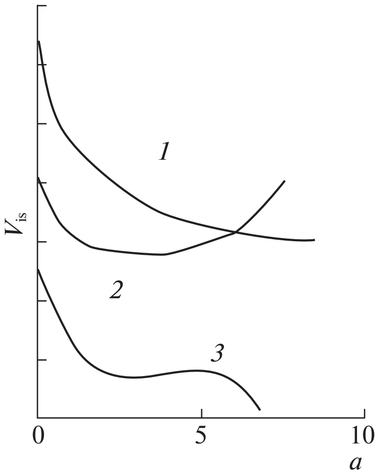

Fig. 3. Possible form of curve $V_{is}(a)$. See denotations in text.

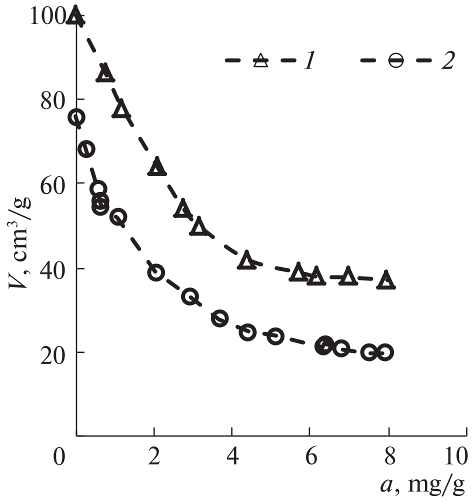

Fig. 4. Dependences of $V_{is}(a)$ for *n*-hexane on (*1*) Psb-1 and (*2*) Psb-Ag at 160°C.

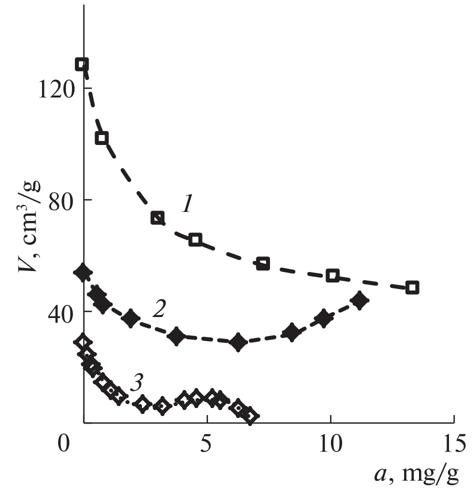

Fig. 5. Dependences of $V_{is}(a)$ for (*1*) methanol at 140°C, (*2*) water at 100°C, and (*3*) water at 140°C and on active carbon AC-Ag.

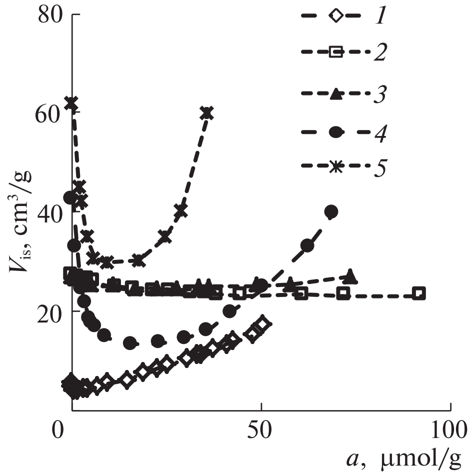

Fig. 6. Dependences of $V_{is}(a)$ for (*1*) *n*-heptane on chitosan 550; (*2*) CCl_4, (*3*) $CHCl_3$, (*4*) 1-propanol, and (*5*) 1-butanol on chitosan Kh-60 at 120°C.

bent, less active centers participate in the sorption process: V_{is} values quickly fall, an area of adsorption on centers that vary little in terms of sorption potential is reached, and V_{is} changes little with filling. This form of dependence $V_{is}(a)$ is observed for substances that are indifferent to the nature of the sorbent's surface under experimental conditions, e.g., nonpolar *n*-alkanes on Psb-1 and Psb-Ag [18] (Fig. 4); methanol on activated carbon modified with silver, AC-Ag [19] (Fig. 5); CCl_4 and $CHCl_3$ on chitosan Kh-60 [20] (Fig. 6); and *n*-octane on silochrome C-120-8,2 [21] (Fig. 7). This form of dependence $V_{is}(a)$ is rarely seen in chromatographic practice; these systems are most often described by a poorly resolved S-shaped dependence of type 3, as exemplified by *n*-heptane on C-120-1,3 [22] (Fig. 7, table 1).

The form of $V_{is}(a)$ of type 2 is observed when the adsorption mechanism changes as the sorbate accumulates on the adsorbent's surface. This curve of $V_{is}(a)$ describes, e.g., the adsorption of water on active carbon AC-Ag at temperatures of up to 100°C [23] (Fig. 5). The filling of activated carbon with water starts from the formation of sorption complex with the most active acidic centers in thin pores, when water molecules can interact with several surface centers simultaneously. This range of filling corresponds to the highest values of V_{is}. The concentration of these centers is usually small, and a subsequent drop in V_{is}

values due to the sorption of less active centers occurs rapidly. The drop then slows down and a range of *a* values is observed in which the value of V_{is} changes little. This may conditionally be considered a range of some homogeneity. With a further increase in the concentration of water on the carbon surface (in this case, at $a > 5$ mg/g (~300 μmol/g)), a drastic rise in the curve $V_{is}(a)$ begins as a result of sorbate–sorbate interaction in the sorption layer and the corresponding sorption of water molecules on sorbed molecules; i.e., the formation of polylayers in the area of primary sorption begins. In micropores, this stage proceeds as capillary condensation.

With an increase in the concentration of water on the carbon surface, the process of physical adsorption is thus replaced by bulk filling. The concentration of sorbate up to the substitution of the filling mechanism is determined by the concentration of primary sorption centers, N_z. The value of N_z has the physical sense of the specific surface of the sorbent for a given sorbate and under specific conditions.

The similar form of type 2 is characteristic of dependence V_{is}(a), which describes the sorption of surface-active substances on swelled polymers, when the accumulation of sorbate on the sorbent's surface due to physical adsorption induces dissolution in the bulk sorbent. The sorption of alcohols on chitosans and polyelectrolyte chitosan and poly(acrylic acid) complexes occurs according to this scenario [24, 25], e.g., 1-propanol and 1-butanol on chitosan Kh-60 (Fig. 7). The form of V_{is}(a) for *n*-heptane on polysaccharide Kh-550 is interesting (Fig. 7): the rise of curve V_{is}(a), which indicates the onset of absorption, starts at a concentration of $a \approx 2–3$ μmol/g; with alcohols, however, the rise begins in the range of 20–30 μmol/g.

Dependence V_{is}(a) of type 3 (Fig. 3) describes the order of filling of an inhomogeneous adsorbent's surface by a sorbate, which also begins with the adsorption of sorbate molecules on the most active sorption centers. The V_{is} values are highest at this stage and then fall, due to sorption on less active centers. Finally, the decline slows and there is a subsequent rise in values, due to the increased contribution from sorbate–sorbate interaction, since sorbate molecules prefer to sorb in the area of the primary sorption complex. Multilayer drops or clusters in this case form on the surface and V_{is} falls at the end of drop formation and the reduction in the vapor pressure of the low-molecular substance over the concave surface. Such S-shaped curves thus indicate the filling of an unhomogeneous sorbent's surface by sorbate with the formation of isolated multilayer clusters in the area of primary sorption. The S-shaped dependence of $V_{is}(a)$ is closely approximated ($R > 0.99$) by a third-rank polynomial of the form $y = ax^3 + bx^2 + cx + d$. The inflection point, which is determined by the second derivative corresponding to zero ($y'' = 0$), corresponds to the onset of the formation of polylayers, and the concentration N_z of primary sorption centers can be estimated from it.

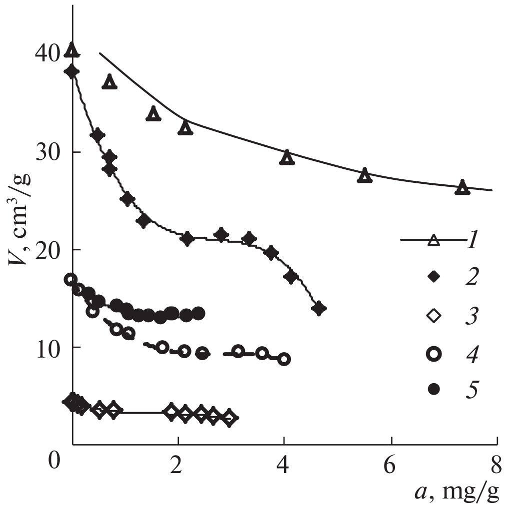

Fig. 7. Dependences of $V_{is}(a)$ for (*1*) methanol and (*2*) *n*-heptane on C120-1,3 at 140°C; (*3*) *n*-octane on silochrome C-120-8,2 at 120°C; (*4*) water on C-120-3,2 (3 nm); and (*5*) water on C-120-3,2 (17 nm) at 140°C.

Island filling of the surface is observed for sorbates that can distinguish the nature of sorption centers of a heterogeneous sorbent, and is the type of filling encountered most often in chromatographic practice. This dependence of $V_{is}(a)$ is observed for, e.g., methanol and water on silver-containing composites based on silochrome C-120 [21, 26, 27] (Fig. 7), which have a high degree of hydrophilicity due to their hydrated silver nanoparticles. With nonpolar *n*-heptane, the S-shaped form of $V_{is}(a)$ is poorly resolved and the value

Table 1. Sorbate–sorbent adsorption systems, temperatures of experiments (*t*,°C), third-rank polynomial coefficients, correlation coefficient (*R*), and concentrations of primary sorption centers (N_z)

Sorbate–sorbent	*t*, °C	*a*	*b*	*c*	*d*	*R*	N_z, μmol/g
n-Heptane–C-1,33 (17 nm)	140	–0.1982	0.9988	–1.7706	4.3403	0.9972	16.8
Methanol–C-1,33 (17 nm)	140	–0.8432	6.7863	–18.643	38.492	0.9964	83.3
Water–C-3,2 (3 nm)	140	–0.3357	2.8132	–7.8889	16.736	0.9985	155
Water–C-3,2 (17 nm)	140	–03753	2.5594	5.5045	16.873	0.9889	126
Water–AC + Ag	160	–0.4565	5.3537	–19.023	26.998	0.9965	217

of N_z for water and methanol N_z is much higher than that of *n*-alkane (*see* table 1).

A change in the operational quantitative and qualitative composition of adsorption centers always alters the form of $V_{is}(a)$. An analysis of $V_{is}(a)$ for water on silver-containing composites C-120-3,2 (3 nm) and C-120-3,2 (17 nm) allowed us to investigate how a change in the state of silver nanoparticles manifests itself in adsorption. It is clear from Fig. 7 that upon changing the mean diameter of silver nanoparticles from 3 to 17 nm, the surface becomes more homogeneous, the S-shaped form is less clear, and the concentration of primary centers falls (*see* table 1). Except for the initial section, however, they are more active over the range of *a* [27] (Fig. 7).

The change in the form of $V_{is}(a)$ for water at the hydrophilic angle of AC-Ag from type 2 to type 3 with an increase in temperature [23] (Fig. 5) clearly shows that the bulk filling of thin pores of carbon with water proceeds at lower temperatures of 100°C; at 160°C, there is no condensation in pores and water is sorbed on carbon to form clusters in the area of primary sorption.

The asymmetry of an elution curve is a very sensitive characteristic of surface heterogeneity. As an example, an increase in asymmetry and peak diffusion of nonspecifically sorbing *n*-alkanes and a reduction in these characteristics for the peaks of specifically sorbing alcohols were observed in [26] upon an increase in the hydrophilicity of a surface of fully hydroxylated silica, due to its modification with silver nanoparticles.

CONCLUSIONS

Depending on the nature of the molecular probe and the experimental conditions using the same sorbent, different sorption scenarios can be implemented and a complete picture of the nature of sorbent can be presented only by using molecular probes of different natures.

Chromatographic characteristics of retention related to the final concentration of sorbate in the gas phase or on a nonhomogeneous sorbent's surface ensure a description of the sequence of sorbent filling by the sorbate, give insight into its structural state under specified conditions, and allow qualitative and quantitative estimates of the surface's inhomogeneity.

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SPELL: 1. bythe, 2. inhomogenous