DETERMINATION OF THE VAPOURS OF ORGANIC SUBSTANCES AND INORGANIC AEROSOLS IN NON-CORROSIVE GASES BY GAS CHROMATOGRAPHY; QUANTITATIVE DYNAMIC SORPTION OF VAPOURS THROUGH A COLUMN OF GRANULATED SORBENT — MECKLENBURG'S EQUATION

Miloslav VANĚČEK and Michael WALDMAN
Institute of Hygiene and Epidemiology, Prague

Received December 6th, 1977

Dedicated to Professor F. Čůta on the occasion of his 80th birthday.

The conditions of quantitative dynamic sorption of organic solvent vapours from inert gases on a column (6 mm diameter) of granulated (1·0—1·2 mm) active charcoal were investigated. The dependence of the time of quantitative sorption on the height of the sorbent column, on physico-chemical properties and the concentration of adsorbate, and on the flow rate of the analyzed gas was followed by recording breakthrough curves. For the evaluation of the efficiency of sorbent columns the equation of dynamic inefficiency of the column was proposed by means of which Mecklenburg's equation was extended to the form enabling the calculation of minimum height of the sorbent bed for the required time of sampling at a given flow rate of the analyzed gas, maximum permissible flow rate of the analyzed gas for the required time of sampling by a column of a given height, and maximum permissible times of the sampling by a column of a given height, for a given flow rate of the analyzed gas.

Maximum permissible times of vapour sampling of some organic solvents are calculated for concentrations $C_g \leqq 10^{-2}C_{g0}$, where C_{g0} is the concentration corresponding to the saturated vapour pressure, a column 2 cm high (225 mg of active charcoal) for flow rates 50, 250, 500, and 1000 $cm^3 min^{-1}$ and minimum height of the sorbent column for vapour sampling for the periods of 10, 20, 40 and 60 min for a flow rate of 500 $cm^3 min^{-1}$. Conditions are given for the determination of the vapours by sampling through a column 2 cm high.

Quantitative dynamic sorption of organic vapours from inert gases and from the atmosphere has already been used for the purposes of gas-chromatographic analysis by a number of authors. Among granulated sorbents mainly active charcoal[1–9], silica gel[10] and also organic polymers[11] and chromatographic supports with stationary phase[12] were used. The proposed adjustment of the sampling columns of active charcoal for the sorption of vapours of the concentrations $C_g \leqq 10^{-2}C_{g0}$ differs considerably from author to author, especially in the shape and the internal diameter of the sampling tubes, granulation of the sorbent, height of the bed, and the preparation of active charcoal. Only a few authors free active charcoal of moisture before sampling using desorption with a stream of inert gas at an elevated temperature[7], achieving thus an increase in the amount of the sorbed vapours per unit of mass of the sorbent. West and coworkers[1] recommend for a 20 minutes' sampling of vapours U-tubes with 200 mg of sorbent and a 1000 cm^3 . . min^{-1} flow rate. Reid and Halpin[9] sorb the organic vapours from 4 to 10 l of air with columns 6 cm high (600 mg of active charcoal), at a 1000—2000 $cm^3 min^{-1}$ flow rate. For a one hour's sampling of hydrocarbons from the air Herbolsheimer[3] recommends columns 5 cm high and a 400 $cm^3 min^{-1}$ flow rate. Only some of these authors have discussed the theoretical and experimental substantiation of the proposed adjustments from the point of view of quantitative retention of the vapours. For example Fraust and coworkers[6,8] used the method of analysis of breakthrough curves for the study of the effect of the flow of the gaseous mixture, concentration and the physico-chemical properties of the adsorbate on the ability of the column to sorb quantitatively, and formulated some empirical relationships. Cropper and Kaminski[12] evaluate the ability to sorb quantitatively in cases of short chromatographic columns with a support and stationary phase on the basis of the maximum permissible volume of the analyzed gas. They express this volume as 4/5 of the retention volume of the carrier gas for a given substance on a given chromatographic material, calculated from the tabulated values of specific retention volumes of the temperature of 25°C. Other authors circumvent this problem by inserting the control column of active charcoal behind the sampling column, thus ensuring the sorption of unretained vapours, if any. Thus, for example, White and coworkers[2] put another equally large control column behind the sampling column 2 cm high (180 mg of active charcoal) and recommend for the analysis of 10 l of air a 500–2500 $cm^3 min^{-1}$ flow rate. Mueller and Miller[4] sorb the vapours of organic compounds from 10 l of air by commercially produced tubes (Mine Safety Appliance Co., Inc.) with two columns, a sampling one with 100 mg, and a control one with 50 mg of active charcoal, using a 1000 $cm^3 min^{-1}$ flow rate. All these authors trap the organic vapours on active charcoal from a gas from which water vapours were not previously eliminated. The sorption of organic vapours on silica gel, after preliminary retention of water vapours by means of the molecular sieve 5A, was described by Whitmann and Johnston[13]. The sampling of organic vapours on small columns with supports and stationary phase from predried air was described by Eggertsen and Nelsen[14] who used Askarite as dessicant in the determination of hydrocarbons, and by Farrington and coworkers[15] who recommended anhydrous potassium carbonate as dessicant in the determination of vapours of polar and non-polar substances in the air.

The results of the study of the effect of the physico-chemical properties of adsorbate, its concentration and the flow rate of the analyzed gas on quantitative dynamic sorption through a column of granulated active charcoal are the subject of this communication. Its aim is the elaboration of objective bases for the proposal of the most suitable conditions of the sampling of gaseous mixtures for gas-chromatographic analysis.

THEORETICAL

During forced axial convection of the carrier gas with a low concentration of organic vapour C_g through an active charcoal bed of height X, continuous decrease of the sorbate concentration takes place in consequence of dynamic sorption until the concentration of sorbed vapours is achieved in the direction of the gas flow in the unit weight of the sorbent, which corresponds to the equilibrium state. The time after which the concentration $C_{gi} = iC_g$, where $0 < i < 1$, appears at the end of the column in the carrier gas, is usually called breakthrough time t_{gi}, in the ref.[19] "ϑ" service life of filter. The dependence of the breakthrough times on the column height, $t_{gi} = f(X)$, so-called Shilov's curve[16] represents the picture of axial velocity of the concentration point C_{gi} through the column at constant flow rate and adsorbate concentration. The dependence of the adsorbate concentration in the gas on time at the column outlet can be recorded as the breakthrough curve. According to Rachinski[17] the dynamic sorption of organic vapours with a convex type of adsorption isotherm can be characterized, till the equilibrium state is attained, by a stage of the formation of the adsorption wave with a subsequent so-called stage of the transfer of the stationary adsorption wave. In the first stage, taking place very shortly after the beginning of the dynamic sorption, the dynamics of the sorption is controled by the distribution of the velocities of the concentration points v_{gi}, (originally[18] labelled as "v_c"), formulated in a general way by Wicke[18]; the relationship when adjusted for experimental application has the form:

$$v_{gi} = \omega/[1 + \varrho(\mathrm{d}C_s/\mathrm{d}C_{gi})]\,S\,. \qquad (1)$$

For this stage the time dependence of the shape of the adsorption front on the sorbent column is characteristic, while the function $t_{gi} = f(X)$ has a general non-linear character. In the second stage, taking place on the column from the moment of the termination of the first stage up to the equilibrium attainment, the dynamics of the sorption is controlled by the uniform velocity of all concentration points, the so-called rate of transfer of stationary adsorption wave v_g (in ref.[18] labelled as "v"), which can be expressed for experimental purposes by the relationship:

$$v_g = \omega C_g/\varrho S C_s\,. \qquad (2)$$

At this stage the shape of the adsorption front passing in the direction of the gas flow through the column is independent of time, while the function $t_{gi} = f(X)$ has a linear character which can be described by the adjusted Mecklenburg's relationship[19]:

$$t_{gi} = K_0(X - X_{gi}) = (X - X_{gi})/v_g\,, \qquad (3)$$

where K_0 can be indicated as the efficiency coefficient of the dynamic sorption (according to the original reference[16] it is indicated as "k" and called "coefficient of service life of the filter") and X_{gi} represents the non-efficient height of the column (in ref.[19] indicated as "h" and called "dead layer"). The interpretation of the parameters of Mecklenburg's relationship[19] on the basis of the analysis of the breakthrough curves has been given by Zikánová[20]. The amount of vapour sorbed at equilibrium, expressed as the adsorbate concentration in unit weight of the sorbent, C_s, can be evaluated with sufficient accuracy from the adjusted Dubinin–Radushkevich equation[21],

$$C_s = W_0 d_T \exp\{-[BT^2/\beta^2]\,[\log(C_{g0}/C_g)]^2\}\,, \qquad (4)$$

using the procedure discussed in our preceding paper[22]. Dubinin-Radushkevich's and Mecklenburg's equations were used by Nelson and Harder[23,24] for the study of the service life of respirator cartridge.

EXPERIMENTAL

Chemicals and Apparatus

Active charcoal (Moravské chemické závody, Ostrava), carbon disulfide a.g., organic solvents a.g., molecular sieve 3A, were treated and purified as in the preceding communication[22]. The apparatus for continuous preparation of defined concentrations of organic vapours, with an in-built chromatograph Argon Pye, type 12103 was from Pye Unicam, Great Britain. The scheme description, calibration of the apparatus and operation conditions of gas chromatographic analyses are also given in the preceding paper[22].

Preparation of Adsorption Columns

Active charcoal (fraction 1·0—1·2 mm), freed from dust and dried, of a weight preliminarily calculated from the required column height and the bulk density 0·4 g . cm^{-3}, was put into a weighed adsorption glass tube[22] of 6 mm I.D. A stream of dry nitrogen was then passed through the tube (flow rate about 1000 cm^3 . min^{-1}) at 250—300°C until constant weight has been achieved (10—15 min). Then the tube was weighed and the accurate mass of the degased active charcoal determined. Then the settling of the active charcoal particles was homogenized with a vibrator, until the bulk density of the sorbent was 0·4 g . cm^{-3} ± 5%, and the prepared column was firmly fixed with brass rings with a net.

Measurement of Adsorption Data

The gaseous mixture of nitrogen with a defined concentration of organic vapours was passed through the tube with the prepared column, placed in a thermostated jacket. During the measurement the concentration of adsorbate in the gaseous mixture was recorded before the inlet and at the outlet of the column. From the recorded peaks breakthrough curves were constructed by plotting the C_{gi}/C_g ratio *versus* time. From the increase of the weight of the adsorption tube the equilibrium concentrations of the adsorbed vapours in the weight unit of the sorbent C_s were determined and then compared with the values calculated according to (*4*) and (*6*). All measurements were carried out at 20 ± 0·2°C.

RESULTS AND DISCUSSION

From the constructed breakthrough curves the time t_{gi} was estimated, during which the outlet concentration attained one tenth of the inlet concentration, $C_{gi} = 0{\cdot}1C_g$. In further text it will be referred to only as breakthrough time t_{gi}.

For the estimation of the measured data from the analytical point of view, this moment (in the ref.[23] indicated as "t_b", 10% breakthrough time) was considered as the end of the quantitativeness of the sorption. Further the time was determined from the breakthrough curves within which the concentration of the adsorbate at the column outlet attained half of the value of the inlet concentration ($C_{gi} = 0{\cdot}5C_g$). This time was labelled $t_{gi} + \Delta t_{gi}$, where Δt_{gi} is the breakthrough time increment. The construction of Shilov's curves from these data is shown in Fig. 1. At an axial flow of the gas mixture with the adsorbate concentration C_g, the flow rate ω through a column of X_1 height and cross-section S, the detector located at the column outlet records the concentration $C_{gl} = 0{\cdot}1C_g$ at the moment t_{1gi} (point H_1). During a dynamic sorption under the same conditions, through a column of height X_2, where $X_2 > X_1$, the detector records concentration $C_{gi} = 0{\cdot}1C_g$ at the time t_{2gi} (point H_2), and the concentration $C_{gi} = 0{\cdot}5C_g$ at the time $t_{2gi} + \Delta t_{2gl}$ (point S_2). Under the assumption that the second stage of the dynamic sorption is achieved it applies that $\Delta t_{1gl} = \Delta t_{2gi} =$ const., *i.e.* the breakthrough time increments are not a function of the column height. For Δt_{gi} the relationships (*5*) and (*6*) apply

$$\Delta t_{gi} = K_0 X_{gi} = X_{gi}/v_g = C_s S \varrho X_{gi}/\omega C_g \tag{5}$$

and

$$t_{gi} + \Delta t_{gi} = K_0 X = X/v_g = C_s S \varrho X/\omega C_g\,. \tag{6}$$

These relationships were used for the evaluation of the non-effective height of the column X_{gi} and of the coefficient of efficiency of dynamic sorption K_0, while the relationship (*6*) may also be used for the determination of the concentrations of the sorbed vapours in the weight unit of the sorbent at equilibrium C_s.

The effect and the physico-chemical properties of the adsorbate and the effect of the flow rate of the gaseous mixture was studied. In a general case X_{gl} is also depen-

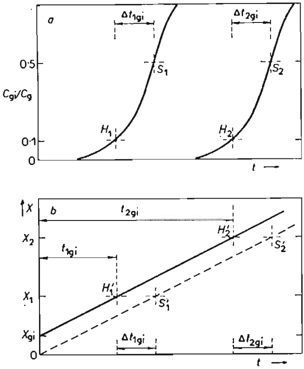

FIG. 1
Evaluation of the Breakthrough Curves

dent on temperature, area and the shape of the perpendicular cross-section of the column, and the fraction of the granulated sorbent used. These parameters were kept constant during the measurements, and therefore their effect is not discussed.

Effect of the Adsorbate Type on the Value of X_{gi}

A set of adsorption tubes containing columns of active charcoal of 2 cm height (225 mg) was prepared. At 500 $cm^3 . min^{-1}$ flow rate the breakthrough curves for CH_2Cl_2, $CHCl_3$ and CCl_4 were recorded at a $2 . 10^{-7}$ g . cm^{-3} concentration of adsorbate. From the breakthrough curves represented in Fig. 2 the breakthrough times $t_{gi} = 22$ min (CH_2Cl_2), $t_{gi} = 115$ min ($CHCl_3$), and $t_{gi} = 250$ min (CCl_4) were determined, and further the breakthrough time increments $\Delta t_{gi} = 9$ min (CH_2Cl_2), $\Delta t_{gi} = 52$ min ($CHCl_3$), and $\Delta t_{gi} = 112$ min (CCl_4). The equilibrium concentrations of the sorbed vapours in weight unit of the sorbent were determined, $C_s = 1{\cdot}32 . 10^{-2}$ g . g^{-1} (CH_2Cl_2), $C_s = 7{\cdot}47 . 10^{-2}$ g . g^{-1} ($CHCl_3$) and $C_s = 1{\cdot}62 . 10^{-1}$ g . g^{-1} (CCl_4). According to the relationship (5) the values of the non-effective column height, $X_{gi} = 0{\cdot}61$ cm (CH_2Cl_2), $X_{gi} = 0{\cdot}62$ cm ($CHCl_3$), and $X_{gi} = 0{\cdot}61$ cm (CCl_4) were determined. It was also checked that in the above experimental conditions the value of X_{gi} is independent of the physico-chemical properties of the adsorbate. For a 500 $cm^3 . min^{-1}$ flow and the adsorbate concentration $2 . 10^{-7}$ g . cm^{-3} the breakthrough curves for various heights of the columns were

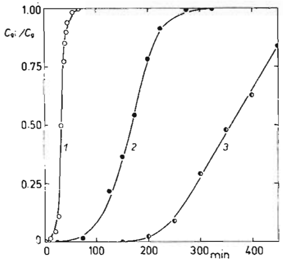

FIG. 2

Breakthrough Curves of Adsorbates of Equal Concentrations

Column height $X = 2$ cm, flow rate $= 500$ $cm^3.min^{-1}$, $C_g = 2 . 10^{-7}$ $g.cm^{-3}$; breakthrough curve of *1* dichloromethane; *2* trichloromethane; *3* tetrachloromethane.

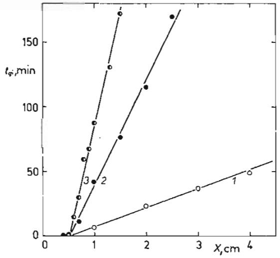

FIG. 3

Dependence of the Duration of Quantitative Sorption t_{gi} on the Column Height for Equal Concentrations of Adsorbates

$C_g = 2 . 10^{-7}$; flow rate $\omega = 500$ $cm^3 . min^{-1}$; *1* dichloromethane, *2* trichloromethane; *3* tetrachloromethane.

also recorded, and Shilov's curves (Fig. 3) were constructed from the measured data. Using the method of least squares the values of the slopes of the curves were determined, further the coefficients of efficiency of the dynamic sorption $K_0 = dt_{gi}/dX = 15\cdot3 \text{ min . cm}^{-1}$ (CH_2Cl_2), $K_0 = 82\cdot2 \text{ min . cm}^{-1}$ ($CHCl_3$) and $K_0 = 180\cdot5 \text{ min . cm}^{-1}$ (CCl_4), and it was confirmed that the value X_{gi} determined by extrapolation of Shilov's curves for $t_{gi} = 0$ is in agreement with the values calculated from the equation (*5*), and hence, that the relationship[20] $K_0 = 1/v_g$ is fulfilled. Analysis of the measured values showed that at constant flow rate and equal concentrations of adsorbates the ratio of the breakthrough times is equal to the ratio of the equilibrium concentrations of the sorbed vapours in the weight unit of the sorbent, *i.e.*, *e.g.*, $t_{gi}(CHCl_3)/t_{gi}(CH_2Cl_2) = C_s(CHCl_3)/C_s(CH_2Cl_2) = 5\cdot7$. The vapours of trichloromethane of $2 \,.\, 10^{-7} \text{ g . cm}^{-3}$ concentration can be sorbed quantitatively with a column 2 cm high almost 6 times longer than the same concentration of the vapours of dichloromethane.

Effect of Concentration of Adsorbate on the Value of X_{gi}

A set of adsorption tubes was prepared, containing sorbent columns 1·5 cm high (170 mg). At a flow rate of $500 \text{ cm}^3 \,.\, \text{min}^{-1}$ the breakthrough curves were gradually recorded for the concentrations of benzene $C_{g1} = 2\cdot4 \,.\, 10^{-7} \text{ g . cm}^{-3}$, $C_{g2} = 7\cdot7 \,.\, 10^{-7} \text{ g . cm}^{-3}$ and $C_{g3} = 1\cdot17 \,.\, 10^{-6} \text{ g . cm}^{-3}$. The obtained breakthrough curves are represented in Fig. 4. Under the mentioned conditions benzene can be sorbed quantitatively (as evident from Fig. 4) in 104 min if the concentration is C_{g1}, at concentration C_{g2} in 44 min, and at concentration C_{g3} in 30 min. For the breakthrough time increments $\Delta t_{gi} = 67$ min (C_{g1}), $\Delta t_{gi} = 31$ min (C_{g2}), and $\Delta t_{gi} = 22$ min (C_{g3}) the following values of X_{gi} were found: for (C_{g1}) $X_{gi} = 0\cdot62$ cm, for (C_{g2}) $X_{gi} = 0\cdot62$ cm, and for (C_{g3}) $X_{gi} = 0\cdot61$ cm. It was checked that the differences in the

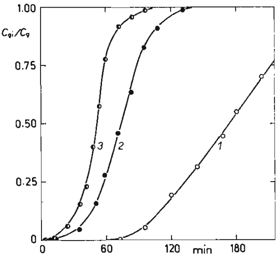

FIG. 4

Breakthrough Curves of Adsorbate (Benzene) for Various Concentrations

Column height $X = 1\cdot5$ cm, flow rate $\omega = 500 \text{ cm}^3\text{-min}^{-1}$; *1* $C_g = 2\cdot4 \,.\, 10^{-7} \text{ g . cm}^{-3}$; *2* $C_g = 7\cdot7 \,.\, 10^{-7} \text{ g.cm}^{-3}$; *3* $C_g = 1\cdot17 \,.\, 10^{-6} \text{ g.cm}^{-3}$.

found values of X_{gi} for individual concentrations were due to random errors, and that the value X_{gi} is not a function of concentration within the concentration range $C_g \leqq 10^{-2}\, C_{g0}$. For convex adsorption isotherm of benzene on active charcoal (the convex character of the adsorption isotherm is fulfilled on active charcoal in the majority of organic adsorbates) it applies that for $C_{g1} < C_{g2}$ is $C_{s1} < C_{s2}$, but $C_{s1}/C_{g1} > C_{s2}/C_{g2}$, and hence $t_{gi}(C_{g1}) > t_{gi}(C_{g2})$. The ratio of the breakthrough times is equal to the ratio of the gradients of the secants of the adsorption isotherm at points C_{s1} and C_{s2}, and hence, for example $t_{gi}(C_{g1})/t_{gi}(C_{g2}) = (C_{s1}/C_{g1})/(C_{s2}/C_{g2}) = 2{\cdot}4$. The time during which the column is capable of sorbing quantitatively increases exponentially with the decrease of the adsorbate concentration in the gaseous mixture and it assumes maximum possible values for concentrations at which the secant of the adsorption isotherm practically merges with the tangent. Shilov's curves for benzene concentrations C_{g1}, C_{g2} and C_{g3}, constructed from breakthrough curves measured at a 500 $cm^3 . min^{-1}$ flow rate and for columns 0·2–4·0 cm high are shown in Fig. 5. From the determined values of gradients, $K_0 = 113{\cdot}6$ min . cm^{-1} (C_{g1}), $K_0 = 47{\cdot}6$ min. cm^{-1} (C_{g2}) and $K_0 = 35{\cdot}0$ min . cm^{-1} it follows how much the quantitative sorption can be prolonged if the height of a column X (where $X > X_{gi}$), is prolonged by 1 cm.

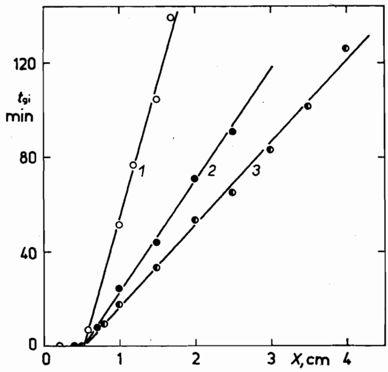

FIG. 5

Dependence of the Duration of Quantitative Sorption of Benzene (t_{gi}) on the Column Height for Various Adsorbate Concentrations

Flow rate $\omega = 500\ cm^3.min^{-1}$; *1* 2·4 . 10^{-7} $g.cm^{-3}$; *2* $C_g = 7{\cdot}7 . 10^{-7}\ g.cm^{-3}$; *3* $C_g = 1{\cdot}17 . 10^{-6}\ g.cm^{-3}$.

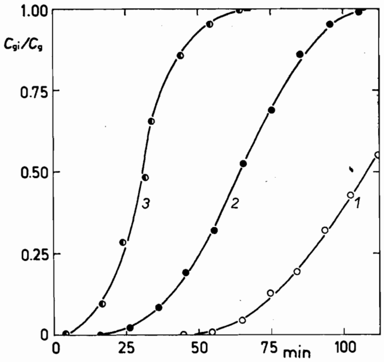

FIG. 6

Breakthrough Curves of Adsorbate (Benzene) at Various Flow Rates

$C_g = 1{\cdot}1 . 10^{-6}\ g.cm^{-3}$, column height $X = 1{\cdot}5$ cm; curve *1* $\omega = 250\ cm^3.min^{-1}$; *2* $\omega = 440\ cm^3.min^{-1}$; *3* $\omega = 860\ cm^3.min^{-1}$.

Effect of the Gas Mixture Flow on the Value of X_{gi}

A set of adsorption tubes with active charcoal beds 1·5 cm high was prepared and the breakthrough curves of benzene of $1{\cdot}1 \,.\, 10^{-6}\,\text{g}\,.\,\text{cm}^{-3}$ concentration were recorded at $\omega_1 = 250\,\text{cm}^3\,.\,\text{min}^{-1}$, $\omega_2 = 440\,\text{cm}^3\,.\,\text{min}^{-1}$ and $\omega_3 = 860\,\text{cm}^3\,.\,\text{min}^1$ flow rates. The measured breakthrough curves and the corresponding Shilov's curves are represented in Figs 6 and 7. At ω_1 flow rate the values $t_{gi} = 74$ min, $\Delta t_{gi} = 34$ min, $X_{gi} = 0{\cdot}46$ cm were found, at ω_2 flow rate the values were $t_{gi} = 38$ min, $\Delta t_{gi} = 26$ min, $X_{gi} = 0{\cdot}59$ cm, and at ω_3 flow rate they were $t_{gi} = 17$ min, $\Delta t_{gi} = 15$ min and $X_{gi} = 0{\cdot}72$ cm. From the given data it is evident that the non-effective column height X_{gi} is a non-linear growing function of the flow rate. The dependence of X_{gi} was then measured in the flow range $40-4000\,\text{cm}^3\,.\,\text{min}^{-1}$ and it is represented in Fig. 8. The obtained dependence of a convex character was called the curve of column non-efficiency and it was approximated by the relationship:

$$X_{gi} = X_{gio}Q\omega/(Q\omega + 1)\,, \tag{7}$$

while the constants $X_{gio} = 1{\cdot}12$ cm and $Q = 1{\cdot}75 \,.\, 10^{-3}\,\text{min}\,.\,\text{cm}^{-3}$ were estimated from the rectified shape of this function, using the method of least squares. The constant X_{gio} is called the limit non-efficient column height, and the constant Q the coefficient of non-efficiency of the column. These constants quantify the suitability of the

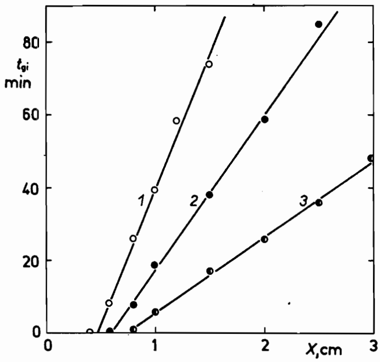

FIG. 7

Dependence of the Duration of Quantitative Sorption of Benzene on the Column Height, for Various Flow Rates

$C_g = 1{\cdot}1 \,.\, 10^{-6}\,\text{g.cm}^{-3}$; *1* $\omega = 250\,\text{cm}^3.\text{min}^{-1}$; *2* $\omega = 440\,\text{cm}^3.\text{min}^{-1}$; *3* $\omega = 860\,\text{cm}^3.\text{min}^{-1}$.

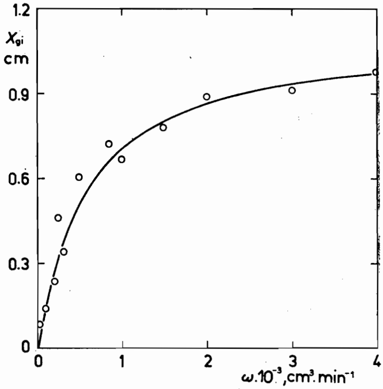

FIG. 8

Dependence of the Non-Efficient Column Height on the Flow Rate — Curve of the Dynamic Non-Efficiency of the Column

Active charcoal, particle size 1·0—1·2 mm, diameter of the sorbent column 6·0 mm.

geometric arrangement of the column bed, *i.e.* its cross-section, size and shape of the particles of the sorbent, for quantitative sorption of vapours at a given flow rate. Putting the relationship (*7*) into the relation (*5*) Mecklenburg's equation was extended to its final form:

$$t_{gi} = (C_s S\varrho / C_g \omega) \{X - [X_{gio} Q\omega / (Q\omega + 1)]\} . \qquad (8)$$

The validity of this relationship was checked by a number of measurements during which the breakthrough curves of some adsorbates were recorded in the concentration range $C_g \leqq 10^{-2}\, C_{g0}$ at various flow rates. The breakthrough time t_{gi}, estimated from the breakthrough curves, was compared with the value calculated from the relationship (*8*). It was checked that the mean error of the calculation of the breakthrough time using relationship (*8*) is 10%. The equation (*8*) permits the characterization of the moment of the termination of the quantitativeness of the dynamic sorption in columns up to 30 cm high, at flow-rates 40–4000 $\text{cm}^3 \,.\, \text{min}^{-1}$.

Analytical Applications

The relationship (*8*) was applied to three types of analytical calculations: *1*) Calculation of the maximum permissible time of vapour sampling by dynamic sorption through a bed of active charcoal of a given height, X, and at a constant flow rate ω, during which the quantitative retention of the organic vapour of maximum $10^{-2}\, C_{g0}$

TABLE 1

Calculated Maximum Sampling Times t_{gi} for Flow Rates $\omega = 50-1\,000\ \text{cm}^3.\text{min}^{-1}$ $X = 2$ cm, 225 mg of active charcoal.

Adsorbate	$C_g{}^a$ μg.cm^{-3}	t_{gi}, min for ω, cm^3.min^{-1}			
		50	250	500	1000
Dichloromethane	16·0	53·5	9·3	4·1	1·8
Trichloromethane	10·0	138·1	24·0	10·7	4·7
Tetrachloromethane	7·5	234·4	40·7	18·1	7·9
Benzene	3·2	300·4	52·2	23·3	10·1
Toluene	1·1	1 006·0	174·8	77·9	33·9
Diethyl ether	18·0	46·4	8·1	3·4	1·6
n-Pentane	17·0	42·8	7·4	3·3	1·4
n-Hexane	5·7	153·5	26·7	11·9	5·2
n-Heptane	1·9	467·2	81·2	36·2	15·8

[a] $C_g = 10^{-2} C_{g0}$.

concentration is ensured. *2*) The calculation of maximum permissible flow rate of the analyzed gas for which a quantitative sorption of organic vapour of a concentration not exceeding $10^{-2}\ C_{g0}$, on columns of height X, is ensured for the required time t_{gi}. *3*) The calculation of the minimum height of the sorbent bed X, for which the quantitative sorption of vapours of a concentration not exceeding $10^{-2}\ C_{g0}$ and at flow rate ω is still ensured for the required time t_{gi}.

In Table I a review is given of maximum permissible times of the sampling of some vapours in columns 2 cm high (225 mg of active charcoal) at four flow rates. These values were calculated from the relationship (*8*), while the necessary values of equilibrium concentrations of the sorbed vapours in a weight unit of sorbent C_s for adsorbates of concentration $10^{-2}\ C_{g0}$ were calculated using equation (*4*) and the procedure employed in the preceding paper[22]. An example of the second type of calculation is given in Table II. For columns 6 cm high (676 mg of active charcoal) the maximum permissible flow rates of the analyzed gas have been calculated for various times of vapour samplings. The values were calculated using the relationship (*9*), obtained from equation (*8*) by explicit expression of the flow rate

$$\omega = \{[(C_g t_{gi} - C_s S X Q \varrho + C_s S X_{gi0} Q \varrho)^2 + 4 C_g C_s S X Q t_{gi} \varrho]^{1/2} / 2 C_g Q t_{gi}\} + \\ + (C_s S X Q \varrho - C_s S X_{gi0} Q \varrho - C_g t_{gi}) / 2 C_g Q t_{gi} \,. \qquad (9)$$

In Table III the minimum column heights of active charcoal have been calculated that guarantee a quantitative sorption for various sampling times at a 500 cm^3.

TABLE II

Calculated Maximum Flow Rates ω for Sampling Time $t_{gi} = 20-120$ min
$X = 6$ cm, 675 mg of active charcoal.

Adsorbate	C_g[a] $\mu g.cm^{-3}$	ω, cm^3.min^{-1} for t_{gi}, min			
		20	40	60	120
Dichloromethane	16·0	355	182	123	62
Trichloromethane	10·0	875	452	307	158
Tetrachloromethane	7·5	1 450	748	509	263
Benzene	3·2	1 840	948	644	332
Toluene	1·1	5 960	3 030	2 050	1 050
Diethyl ether	18·0	310	159	107	54
n-Pentane	17·0	287	147	99	50
n-Hexane	5·7	967	500	343	178
n-Heptane	1·9	2 820	1 440	981	507

[a] $C_g = 10^{-2} C_{g0}$.

. min^{-1} flow rate. The values of the column heights were calculated from equation (*10*) obtained from equation (*8*) on expressing the column height explicitely:

$$X = (C_g \omega t_{gi}/C_s S \varrho) + [X_{gi0} \varrho \omega/(\varrho \omega + 1)] \,. \tag{10}$$

The values presented in the Tables I, II and III are calculated for the analyzed gas in the absence of water vapours.

The water vapours present in the analyzed gas are sorbed simultaneously with the vapours of organic solvents, thus decreasing the equilibrium concentrations of the sorbed vapours in the mass unit of sorbent C_s significantly, and hence also the efficiency coefficient of the dynamic sorption K_0.

Since in a real analyzed gas a certain amount of humidity is always present, it was necessary to predry it with a molecular sieve. For the determination of the vapours of organic compounds listed in Tables I, II and III the molecular sieve 3A is suitable, because this type of sieve does not significantly sorb the organic vapours analytically.

Determination Procedure

The data in Table I were used for the proposal of the determination of organic solvent vapours based on sampling by dynamic sorption in a column of active charcoal, 2 cm high. About 250 mg of active charcoal is introduced into a glass tube of 6 mm internal diameter and 6 cm length and the settling of the particles is homogenized

TABLE III

Calculated Minimum Column Heights X for Sampling Time $t_{gi} = 10-60$ min $\omega = 500$ cm^3 min^{-1}, $X = 1$ cm $= 113$ mg of active charcoal.

Adsorbate	C_g[a] μg.cm^{-3}	X, cm for t_{gi}, min			
		10	20	40	60
Dichloromethane	16·0	4·9	7·7	14·8	21·4
Trichloromethane	10·0	1·1	3·3	6·1	8·8
Tetrachloromethane	7·5	1·3	2·2	3·8	5·4
Benzene	3·2	1·2	1·8	3·1	4·3
Toluene	1·1	0·7	0·9	1·3	1·7
Diethyl ether	18·0	4·6	8·8	17·0	25·2
n-Pentane	17·0	5·0	9·4	18·4	27·3
n-Hexane	5·7	1·8	3·0	5·5	8·0
n-Heptane	1·9	0·9	1·3	2·2	3·0

[a] $C_g = 10^{-2} C_{g0}$.

with a vibrator so that eventually a column 2 cm high is obtained. The column is then fixed with brass rings and nets. Active charcoal is degassed with a nitrogen stream at 250–300°C for 15 min. An allonge of 1·5 cm internal diameter, containing the molecular sieve 3A, is connected with the adsorption tube, and the analyzed gas is sucked through at a selected flow rate for maximum permissible time t_{gi}, or shorter (Table I). The quantity of the molecular sieve is selected according to the volume of the analyzed gas, 100 mg of the molecular sieve per 1 000 cm^3 of gaseous mixture being satisfactory (the equilibrium concentration of the water vapour sorbed in the sieve is $1{\cdot}94 \,.\, 10^{-1}$ g $H_2O \,.\, g^{-1}$ for 90% relative humidity). The desorption of the retained vapours of higher-boiling solvents is carried out with carbon disulfide at room temperature, and of the vapours of lower-boiling solvents with a stream of inert gas at an elevated temperature. The desorbed vapours are determined gas chromatographically. The operation procedures for desorption and chromatographic analyses are given in the preceding paper[22].

We thank Dr E. Smolková, Department of Analytical Chemistry, Charles University, for her constant interest in the solution of the problem of analytical application of the adsorption of organic vapours by granulated sorbents. Her remarks and suggestions contributed considerably to the greater accuracy of our formulations and the evaluation of our results.

LIST OF SYMBOLS

B	constant (K^{-2})
C_g	concentration of adsorbate in gas phase ($g.cm^{-3}$)
C_{gi}	concentration point in gas phase ($g.cm^{-3}$)
C_{g0}	concentration of adsorbate in gas phase corresponding to the saturated vapour pressure at temperature T ($g.cm^{-3}$)
C_s	concentration of adsorbate in weight unit of sorbent ($g.g^{-1}$)
d_T	density of liquid adsorbate at temperature T ($g.cm^{-3}$)
K_0	efficiency coefficient of dynamic sorption ($min.cm^{-1}$)
Q	constant of non-efficiency of the column ($min.cm^{-3}$)
S	cross-section of the sorbate column (cm^2)
T	adsorption temperature (K)
t_{gi}	breakthrough time (the moment when $C_{gi}/C_g = 0{\cdot}1$) (min)
Δt_{gi}	increment of the breakthrough time (min)
v_g	uniform rate of movement of the concentration points C_{gi} at the stage of the transfer of the stationary adsorption wave ($cm.min^{-1}$)
v_{gi}	rate of movement of the concentration points C_{gi} at the stage of formations of adsorption wave ($cm.min^{-1}$)
W_0	limit adsorption space of sorbent ($cm^3.g^{-1}$)
X	height of the sorbent column (cm)
X_{gi}	non-efficient height of the sorbent column (cm)
X_{gi0}	limit non-efficient height of the sorbent column (cm)
β	affinity coefficient (*1*)
ϱ	bulk density of sorbent ($g.cm^{-3}$)
ω	flow rate of the gaseous mixture ($cm^3.min^{-1}$)

REFERENCES

1. West W. P., Sen B., Gibson N. A.: Anal. Chem. *30*, 1390 (1958).
2. White D. L., Taylor G. D., Mauer A. P., Kupel R. E.: Amer. Ind. Hyg. Assoc. J. *31*, 225 (1970).
3. Herbolsheimer R.: Städtehygiene *23*, 280 (1972).
4. Mueller F. X., Miller A. J.: International Laboratory Chromatography July/August, 34, 1974.
5. Tatsuo Kato: Bunseki Kagaku *15*, 14 (1966); Chem. Abstr. *64*, 14 850 g (1966).
6. Fraust C. L., Hermann R. E.: Amer. Ind. Hyg. Assoc. J. *30*, 494 (1969).
7. Herbolsheimer R., Funk L., Drasche H.: Staub-Reinhalt. Luft. *32*, 407 (1972).
8. Fraust C. L., Hermann R. E.: Amer. Ind. Hyg. Assoc. J. *27*, 68 (1966).
9. Reid H. F., Halpin W. R.: Amer. Ind. Hyg. Assoc. J. *29*, 390 (1968).
10. Altshuller A. P., Clemons C. A.: Anal. Chem. *34*, 466 (1962).
11. Williams F. W., Umstead M. E.: Anal. Chem. *40*, 2232 (1968).
12. Cropper F. R., Kaminski S.: Anal. Chem. *35*, 735 (1963).
13. Whitmann N. E., Johnston A. E.: Amer. Ind. Hyg. Assoc. J. *25*, 464 (1964).
14. Eggertsen F. T., Nelsen F. M.: Anal. Chem. *30*, 1040 (1958).
15. Farrington P. S., Pecsok R. L., Meeker R. L. Olson T. J.: Anal. Chem. *31*, 1512 (1959).
16. Shilov N. A., Lepin L. K., Voznesenskii S. A.: Kolloid-Z. *49*, 288 (1929).
17. Rachinskii V. V.: *Vvedenie v Obshchuyu Teoriyu Dinamiky Sorbtsii i Khromatografii*, p. 52. Izd. Nauka, Moscow 1964.
18. Wicke E.: Kolloid-Z. *86*, 295 (1939).
19. Mecklenburg W., Kubelka P. Z.: Z. Elektrochem. *31*, 488 (1925).
20. Zikánová A.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1965.
21. Dubinin M. M.: Chem. Rev. *60*, 235 (1960).
22. Waldman M., Vaněček M.: This Journal *43*, 2905 (1978).
23. Nelson G. O., Harder C. A.: Amer. Ind. Hyg. Assoc. J. *35*, 391 (1974).
24. Nelson G. O., Harder C. A.: Amer. Ind. Hyg. Assoc. J. *37*, 205 (1976).

Translated by Ž. Procházka.