CHROM. 5605

DISTURBING PHENOMENA IN THE MEASUREMENT OF SMALL SURFACE AREAS BY THE DYNAMIC DESORPTION METHOD

D. KOUŘILOVÁ AND M. KREJČÍ

Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

SUMMARY

Thermal diffusion as a disturbing phenomenon in the measurement of small surface areas by the dynamic desorption method is described. The origin of the blank response caused by thermal diffusion is described for the cooling of the measuring column containing the sample in a bath of liquid nitrogen. The influence of the flow rate of the mixture of gases, dead volume of the column and composition of the gaseous mixture on the value of the blank response was studied.

INTRODUCTION

If changes in temperature occur in chromatographic systems, a base-line disturbance is noticed. The disturbance is often caused by the change in the mobile phase flow rate, and sometimes by a thermal diffusion process in which the fractionation of the components contained originally in the mobile phase occurs. This phenomenon is known in liquid chromatography[1] and is sometimes utilized intentionally[2-4].

Disturbing phenomena in the measurement of small surface areas in relatively large volumes of gases by the chromatographic dynamic desorption method were studied in our work. The dynamic desorption method, which is simple from the viewpoint of the apparatus, precise and rapid, was used for the determination of the specific surface areas of flat materials, consisting in this work of metal plates from the tubes of boilers[5], pieces of leather and wood or papers[6]. In the measurement of materials with small surface areas, when adsorption tubes with relatively large volumes must be used as in our case, additional changes in the sorbate concentration in the mixture of gases[6-8] occur owing to thermal diffusion, which increase the concentration changes caused by the adsorption of the sorbate in the measured sample. In contrast to previous papers[7,8] in which a modification of the method for the suppression of the undesirable phenomena was selected, conditions were found such that the undesirable phenomena occurred to the least extent and such that the contribution of the blank response[6] could be determined. When determining the contribution of the blank response, the specific surface area was assumed to be constant over the whole area of the investigated material, and, as a result of this, the multiples of the area studied are also multiples of the specific surface area of the material.

THEORETICAL

The origin of the blank response caused by thermal diffusion is described for the cooling of the column in a liquid nitrogen bath. A radial temperature gradient, variable with time, originates in the column at its immersion into the cooling bath. A radial gradient of concentrations originates owing to thermal diffusion in such a way that the concentration of a sorbate is higher than the original concentration near the column wall in the region of the lower temperature, and lower than the original concentration in the column centre. Also, the concentration gradient is variable with time. Regarding the fact that the linear velocity of the flow of the mixture is not constant over the whole column section, the concentration gradient is not transferred into the detector with the same velocity. The composition of the gases leaving the column changes with time. The longitudinal temperature gradient originates at the column outlet at the point of its immersion into the cooling bath, and further separation of the components of the gaseous mixture owing to the thermal diffusion takes place there.

The magnitude of the thermal diffusion effect depends on the value of the concentration gradient obtained and its transfer into the detector. The radial gradient of concentrations caused by the column cooling, the probable profile of linear velocities in the column and changes in the concentration of the gases in the mixture leaving the column caused by the radial temperature gradient were calculated for a column with a capillary inlet for the gaseous mixture at its centre, I.D. 0.9 cm and length 10 cm, and for the mixture containing 28% (v/v) of nitrogen and 72% (v/v) of hydrogen.

The changes in the thermal conductivity of the gaseous mixture with temperature were neglected in the calculations and the actual course of the temperature gradient was replaced by a linear one. The radial temperature gradient, variable with time, was replaced by its mean value in the limited time interval. Mean temperatures near the column wall ($T = 149°\mathrm{K}$) and at the column centre ($T' = 212°\mathrm{K}$) were determined experimentally and the mean temperature in the column ($\bar{T} = 178°\mathrm{K}$) was calculated[9].

The difference between the concentrations of the sorbate at the column wall and centre, expressed in molar fractions, which is obtained in the equilibrium state, was calculated from the relation[10]:

$$\Delta c' = k_T(\bar{T}) \ln\left(\frac{T}{T'}\right) \qquad (1)$$

where $k_T(\bar{T})$ is the thermal diffusion ratio for temperature $\bar{T}$ and nitrogen concentration $c = 0.28$. The thermal diffusion ratio was calculated[11] to a first approximation for the Lennard-Jones (6-12) potential, $k_T(\bar{T}) = 6.72 \times 10^{-2}$. By substituting $k_T(\bar{T})$ in eqn. 1, $\Delta c' = 2.35 \times 10^{-2}$ is obtained. Assuming the temperature gradient to be linear, the differences in the concentration of nitrogen between the column centre and various radial distances, r, from it were calculated. The maximum deviation from the linear course found was about 5%. That is the reason for describing the concentration profile as a linear function of the radial distance:

$$\Delta c(r) = (6.7r - 1.845)\cdot 10^{-2} \tag{2}$$

where $\Delta c(r)$ is the deviation of the nitrogen concentration from its original concentration in the mixture at a radial distance r.

The transfer of the radial concentration gradient into the detector is dependent on the distribution of linear velocities of the mixture of gases along the column radius.

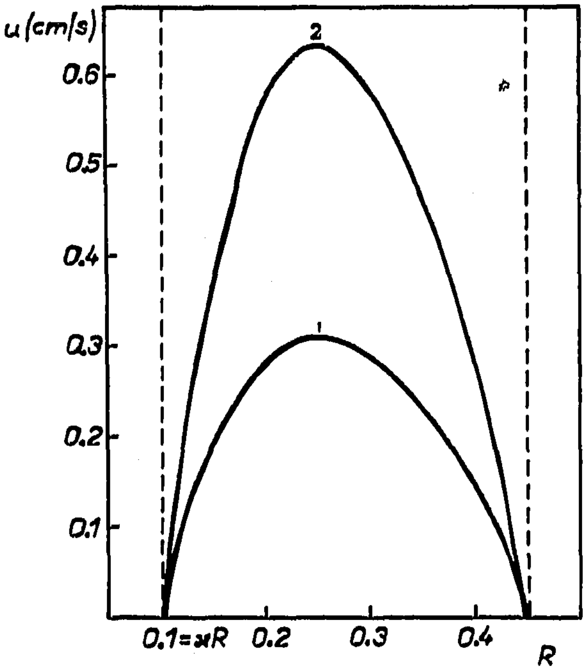

Fig. 1. The profiles of linear velocities in the column calculated according to eqn. 3. (1) $F = 0.125$ ml/sec; (2) $F = 0.250$ ml/sec.

The flow is anticipated to be laminar ($(R_e) < 4.1$) in our case (column with the capillary inlet of gases in its centre, length 10 cm, I.D. 0.9 cm, flow rate of the mixture of gases $F = 0.06$–1.25 ml/sec). The following relation[12] holds for the distribution of the velocities at laminar flow of the fluid through the circular ring with diameters R, κR:

$$u(r) = \frac{2F}{\pi R^2}\cdot\frac{1 - \left(\frac{r}{R}\right)^2 + \frac{1-\kappa^2}{\ln(1/\kappa)}\cdot\ln\left(\frac{r}{R}\right)}{(1-\kappa^4) - \frac{(1-\kappa^2)^2}{\ln(1/\kappa)}} \tag{3}$$

The inlet length necessary for the establishment of a parabolic profile of the velocities was calculated[13] ($L_e = 0.13$ cm). Linear velocity profiles of the given column at the flow rates of the gaseous mixture, $F = 0.125$ and 0.250 ml/sec, calculated according to eqn. 3 are shown in Fig. 1.

Since along the column cross-section the velocity of the gaseous mixture is not constant, the concentration gradient is transferred into the detector with various velocities. It is obvious from Fig. 1 that the same velocity u_i is obtained at a radius r_i where the sorbate concentration is c_i and at a radius r_j where the concentration of the sorbate is c_j. The molecules of the gaseous mixture from these regions will reach the detector in time t_i:

$$t_i = \frac{L}{u_i} + t_k \tag{4}$$

where L is the column length and t_k is the time in which the gaseous mixture passes through the space between the column and detector. The mixture with the concentration c_{t_i} passes through the detector in time t_i:

$$c_{t_i} = c_0 + \Delta c_{t_i}$$

$$\Delta c_{t_i} = \frac{1}{R} \int_{r_0}^{r_i} \Delta c(r) \mathrm{d}r + \frac{1}{R} \int_{r_0}^{r_j} \Delta c(r) \mathrm{d}r \tag{5}$$

where the function $\Delta c(r)$ is given by eqn. 2, r_i and r_j are the radii, where $u = u_i$ ($r_i < r_j$). By substituting for $c(r)$ and integrating, the following expression is obtained:

$$\Delta c_{t_i} = 0.022\ (0.252 + 3.35\ r^2 - 1.845\ r) \tag{6}$$

Δc_{t_i} were calculated for various t_i and the graph of the dependence of $\Delta c = \mathrm{f}(t)$ was plotted for a flow rate of the gaseous mixture of $F = 0.125$ ml/sec (Fig. 2). The graph in Fig. 2 shows the changes in the concentration of the gaseous mixture, which are caused by the radial temperature gradient in the column during the cooling.

A longitudinal gradient, in addition to the radial temperature gradient, originates in the column at the point of its immersion into the cooling bath. Owing to this gradient, further changes occur in the concentration of the mixture of the gases

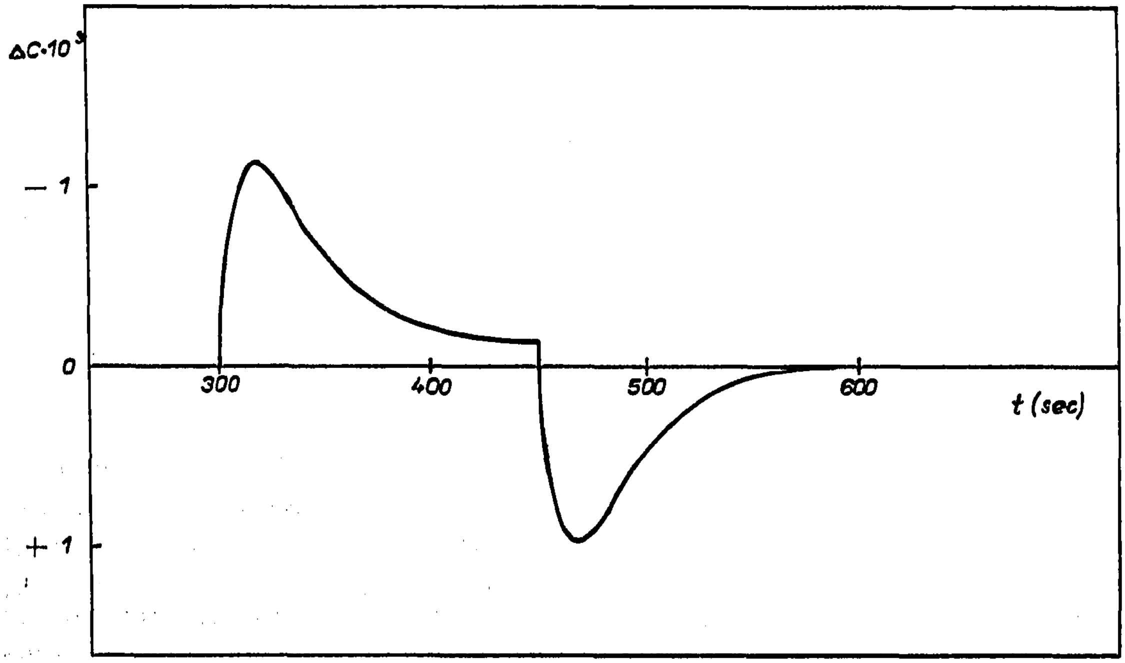

Fig. 2. The changes in the concentration of the gaseous mixture caused by radial temperature gradient in the column during cooling. $F = 0.125$ ml/sec.

flowing to the detector. If the gaseous mixture flows along the temperature gradient, then the nitrogen volume passing through the column cross-section is given by the sum of the volume transferred by the flow, concentration and thermal diffusion[14,15]. Until the stationary state is established, the transferred volume is not constant along the whole length of the column and also the composition of the gaseous mixture entering the detector changes with time. The nitrogen concentration increases in the region of lower temperature inside the column and decreases in the region of higher temperature. At first, the mixture enriched with hydrogen and later with nitrogen enters the detector. As soon as one equilibrium state is established, the mixture of the gases with the original concentration passes through the detector and the longitudinal concentration gradient, which was calculated[15] for various flow rates of the gaseous mixture and is shown in Fig. 3, originates in the column. The changes in nitrogen concentration in the gaseous mixture entering the detector before the establishment of the equilibrium state are proportional to the magnitude of this gradient.

The resulting changes in the concentration of the gaseous mixture entering the detector are given by the sum of the changes caused by the thermal diffusion originating as a result of the radial and longitudinal temperature gradients.

The response is obtained during the column cooling even if no adsorption occurs. That part of the curve is designated as positive which corresponds to the decrease in nitrogen concentration in the mixture of gases during the column cooling.

The phenomena taking place during the column heating are somewhat different. If the stationary state is established during the column cooling, a longitudinal concentration gradient (Fig. 3) exists in the column. During the column heating, a radial temperature gradient is established in the column which leads to the radial concentration gradient. In the column centre, in the region of lower temperature, the nitrogen concentration increases; near the walls, in the region of higher temperature, it de-

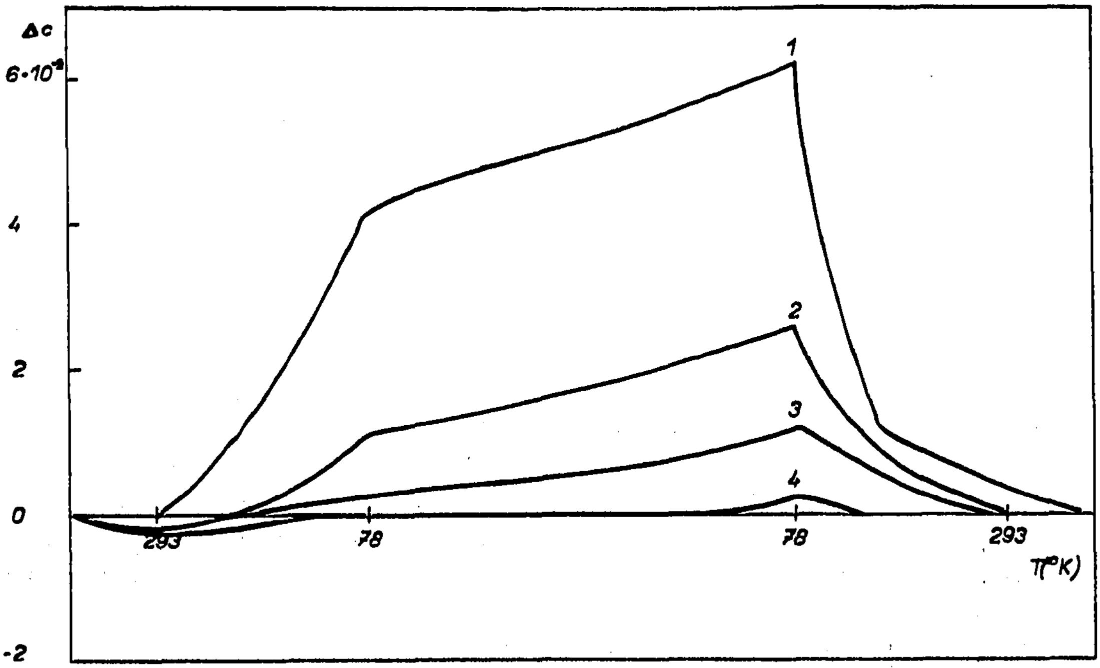

Fig. 3. Longitudinal concentration gradient caused by longitudinal temperature gradient in the column. (1) F = 0.06 ml/sec; (2) F = 0.125 ml/sec; (3) F = 0.250 ml/sec; (4) F = 1.25 ml/sec.

creases. At the same time, a decrease in the longitudinal temperature gradient occurs and thus also a decrease in the longitudinal concentration gradient. At first, an increased concentration of nitrogen and later of hydrogen exists in the mixture of gases leaving the column.

Further, the effects of changes in the flow rate of the gaseous mixture, the dead volume of the column and the concentration of the mixture of gases on the magnitude of the concentration changes caused by thermal diffusion were studied.

The changes in the concentration of the gases leaving the column will be influenced by the flow rate of the gaseous mixture. The magnitude of the concentration gradient which is established along the column due to the longitudinal temperature gradient increases with the decreasing velocity of the flow of the mixture of gases and approaches the maximum value which would be obtained in the static system in the equilibrium state. The dependence of the concentration gradient caused by the longitudinal temperature gradient on the velocity of the flow is obvious from Fig. 3. The changes in the concentration of the mixture of the gases entering the detector will change in a similar way. The value of the radial concentration gradient will depend also on the velocity of the flow of the gas. A certain time is necessary for the establishment of the stationary state described by eqn. 1.

Also, the dead volume of the column affects the values of the concentration changes caused by thermal diffusion. If the column radius changes, changes in the radial temperature gradient take place. The value of the difference in the temperatures between the column wall and centre and the velocity with which the temperature of the bath is achieved in the column centre change. The following relation[16] was derived for the dependence of the value of the temperature gradient on the column radius:

$$T = \frac{\beta}{4\gamma} \cdot r^2 \tag{7}$$

where β is the linear velocity of the column cooling and γ is the temperature diffusivity (thermal conductivity/density × specific heat).

The change in the concentration gradient occurs at the same time as the change in the temperature gradient. The dependence is given by eqn. 1. The time necessary for reaching the bath temperature in the column centre also increases with increasing column radius.

The dead volume of the column is also changed when the amount of measured material is increased.

The value of the concentration gradient caused by thermal diffusion also depends on the original composition of the gaseous mixture. The graph of the dependence is represented by the curve running through a maximum; for the mixture nitrogen–hydrogen the maximum is reached at a concentration of about 45% (v/v) of nitrogen. The mixture with a concentration of 5–30% (v/v) of nitrogen (the range of the validity of the B.E.T. equation) is used for the measurement of surface areas. In this range of concentrations the concentration gradient increases with increasing concentration of nitrogen.

When measuring small surface areas in columns with relatively large dead volumes, the total response during column cooling is the sum of the blank response caused by thermal diffusion and the response proportional to the nitrogen adsorption on the measured material. Two cases may occur during the measurement: the value of the response caused by thermal diffusion remains constant during the experiment and the column dead volume changes only slightly with the change in the surface area measured or the value of the blank response changes during the experiment and the column dead volume also changes with the change in the surface area measured.

The determination of the contribution of the blank response in both cases and the use of the method for the measurement of the surface areas of corroded layers, chromatographic papers and pieces of leather were described earlier[6].

EXPERIMENTAL

The measurement of the blank response caused by thermal diffusion

The apparatus for the determination of specific surface areas of adsorbents, manufactured in the Institute of Instrumental Analytical Chemistry[17,18], was used for the measurement of the blank response caused by thermal diffusion during column cooling or heating. Empty glass tubes of four types with different diameters, x (Fig. 4) were used in place of the columns packed with measured materials. Nitrogen was used as a sorbate and hydrogen as carrier gas. Liquid nitrogen was used in the cooling bath. The same procedure as in the measurement of the surface areas of adsorbents by the dynamic desorption method was used for this measurement.

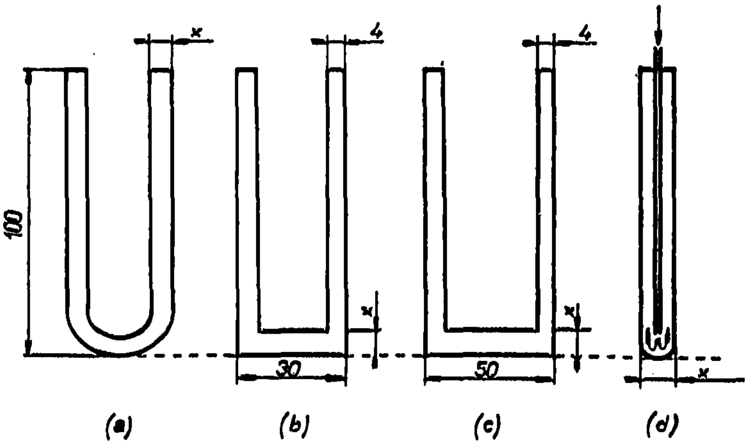

Fig. 4. Column types used for the measurement of the blank response. Dimensions in mm.

The measurement of temperature changes

For the column with the capillary inlet for the gaseous mixture in the centre (d-type), the changes in the temperatures of the column wall and centre during cooling and heating were measured as well as the course of the difference between the temperatures of the column centre and wall. A dual thermocouple (copper–constantan) was used for the measurement, and the thermoelectric voltage of the thermocouple was measured by means of an EZ 3 recording millivoltmeter (Laboratory Equipment, Prague, Czechoslovakia).

When measuring the temperature of the column wall and centre, one contact of each thermocouple was placed on the internal side of the column and in the centre of the column on the capillary inlet, and the other one in the bath of crushed ice and water. When measuring the difference between the temperatures of the column centre and wall, the thermocouple contacts were placed on the internal side of the column and on the capillary inlet. The thermocouple calibration was carried out in such a way that one contact was kept at 0° and the other at 100°, —78° or —195°.

RESULTS AND DISCUSSION

The change in the temperature near the column wall and centre and the course of the difference between the temperatures of the wall and centre during cooling and heating were measured for the column with the capillary inlet of the gaseous mixture in the centre. The mean temperatures of the column wall and centre during the cooling were discussed in the THEORETICAL section. During the heating the mean temperature near the column wall is $T = 177°\text{K}$ and in the centre $T' = 166°\text{K}$. The course of the difference between the temperatures of the column wall and centre is shown in Fig. 5. The maximum difference in the temperatures obtained on column cooling ($\Delta T_C^{\text{max.}} = 125°\text{K}$) is higher than that on heating ($\Delta T_H^{\text{max.}} = 29°\text{K}$) but the time needed for balancing the temperatures is shorter during column cooling ($t_C = 154$ sec, $t_H = 530$ sec). The mean value of the temperature difference is $\Delta T = 53°\text{K}$ during cooling and $\Delta T = 10°\text{K}$ during heating. As relatively rapid changes in the temperature were measured, the time constant of the thermocouple and recorder may distort the results of the measurement.

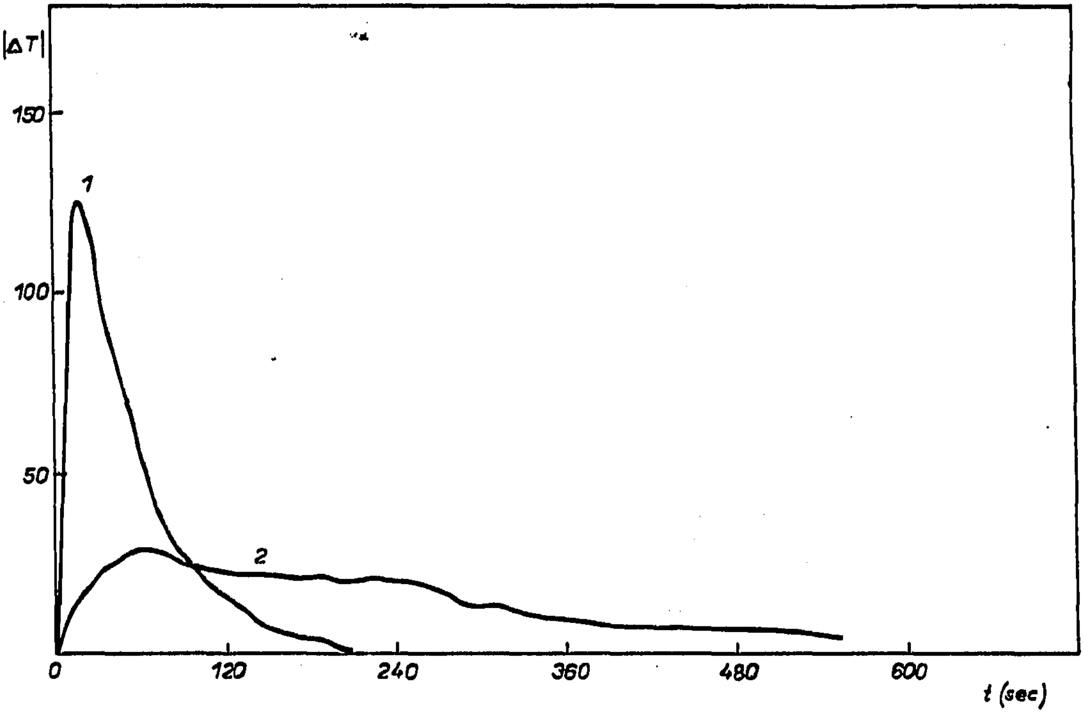

Fig. 5. The course of the difference of the temperatures between the wall and centre of the tube. (1) column cooling; (2) column heating.

It was found that the temperature difference did not change with the change in

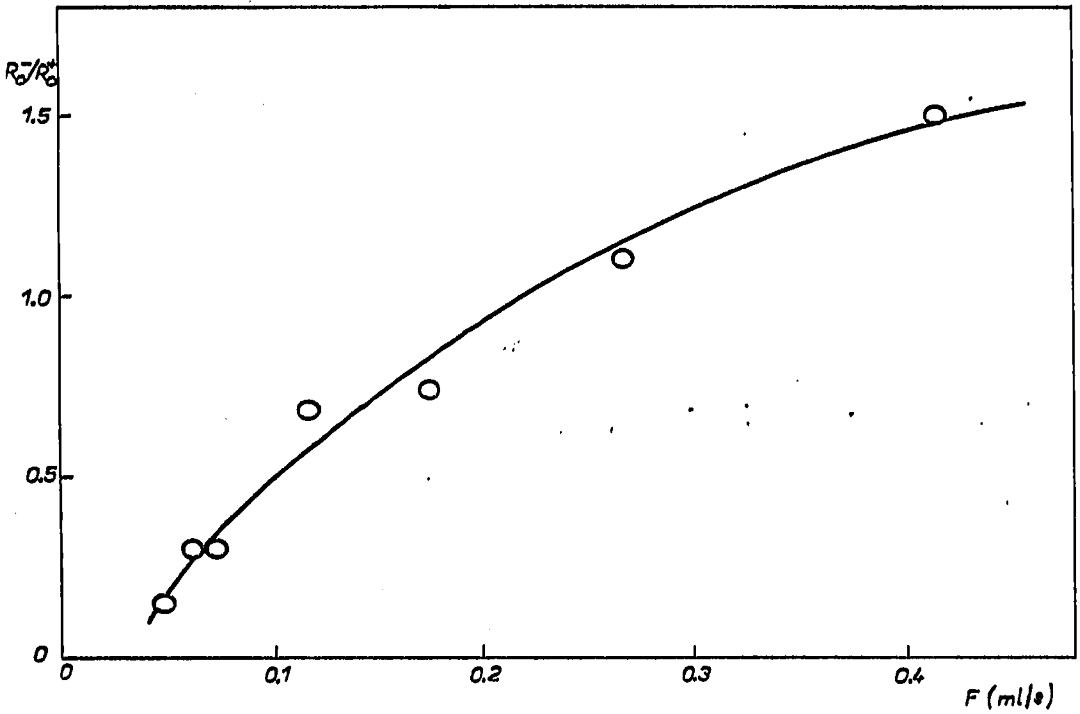

Fig. 6. The dependence of the ratio of the values of the negative and positive parts of the blank response during cooling on the velocity of the flow of the mixture for a U-tube (V_D = 0.6 ml).

the flow rate of the gaseous mixture in the region studied (F = 0.06–1.25 ml/sec). The time needed for balancing the temperatures between the column centre and wall also did not change.

The value of the radial gradient of the temperature and the time needed for balancing temperatures affect the value of the radial concentration gradient and its transfer into the detector. The contribution of the radial concentration gradient to the blank response was calculated with the aid of the relations presented in the THEORETICAL section. The result is shown in Fig. 2. The maximum decrease in nitrogen concentration is 1.1×10^{-3} molar fractions of nitrogen.

Owing to the longitudinal temperature gradient, an increase in the nitrogen concentration occurs in the column which is cooled, while in the mixture of the gases leaving the column the nitrogen concentration decreases. The decrease in the nitrogen concentration in the gaseous mixture entering the detector is proportional to the increase in the nitrogen concentration in the column. The longitudinal concentration gradient which is established in the column and inlet tubes in the stationary state is shown in Fig. 3. The maximum nitrogen concentration occurs, according to Fig. 3, on the column outlet, and the concentration decreases towards the column inlet and acquires values lower than c_0 at higher flow rates of the gas. At first the mixture with the decreased, and later with the increased, nitrogen concentration, and after the establishment of the stationary state the mixture with the original composition, will enter the detector. The maximum deviation of the concentration in the stationary state from the original composition is dependent on the flow rate of the gas. $\Delta c = 6.2 \times 10^{-2}$ was calculated for the lowest flow rate used (F = 0.06 ml/sec) and $\Delta c = 9.15 \times 10^{-2}$ for $F = 0$ (static system). The contribution of the longitudinal temperature gradient to the blank response will obviously predominate at low flow rates of the gas. The value of the concentration change caused by the longitudinal temperature gradient will also be influenced by the volume contraction of the gas in the column when it is immersed in the cooling bath, which will decrease the flow rate. The maximum decrease in the nitrogen concentration, $\Delta c = 8.7 \times 10^{-2}$, was found from the experimental curves measured during column cooling.

The dependence of the height of the positive part of the chromatographic curve on the flow rate of the mixture of gases during column cooling and heating was investigated for the column with the capillary inlet of the gaseous mixture in its centre. The height of the curve was expressed relative to the height of the calibration curve. The course of the dependence is different for column cooling and heating owing to the different course of the thermal diffusion processes taking place in the column during its cooling and heating. During column cooling, the height of the curve increases with decreasing flow rate for $F > 0.2$ ml/sec, passes through the maximum for $F = 0.2$ ml/sec and decreases at lower values of F. The decrease is obviously due to the concentration diffusion which causes the decrease in the concentration gradient caused by thermal diffusion, and its influence increases with decreasing flow rate. The dependence may be described by the empirical equation:

$$h = 3.65 \cdot e^{-2.0\,F} \cdot F^{0.5} \tag{8}$$

During heating, the height of the curve increases with decreasing carrier gas flow rate over the whole range of the investigated flow rates. The empirical function was found for the dependence:

$$h = 0.066 \cdot F^{-0.7} \tag{9}$$

The dependence of the value of the positive part of the blank response, expressed as the volume of the sorbate, on the flow rate of the gas was investigated for this column ($V_D = 4.6$ ml), a-type column ($V_D = 0.6$ ml) and b-type column ($V_D = 3.7$ ml). The dependence has again a different course for column cooling and heating. The dependence may be described during column heating for all the three columns by the following relation:

$$R_0 = a \cdot F^{-1} \tag{10}$$

where a is the constant for a certain column and composition of the gaseous mixture: $a = 0.034$ ml²/sec for an a-type column; $a = 0.042$ ml²/sec for a b-type column; and $a = 0.058$ ml²/sec for a d-type column.

The gaseous mixture containing 24% (v/v) of nitrogen in hydrogen was used for the measurement in the first two cases, and the gaseous mixture containing 28% (v/v) of nitrogen in hydrogen in the third case.

The dependence of the blank response on the flow rate of the mixture of gases during column cooling was expressed by the function:

$$R_0 = b \cdot e^{-nF} \tag{11}$$

where b and n are the constants for a particular column and composition of the gaseous mixture. For an a-type column, $b = 0.065$ ml and $n = 1.6$ sec/ml; and for a b-type column, $b = 0.22$ ml and $n = 3.0$ sec/ml. For a d-type column, the dependence again passes through a maximum at $F = 0.2$ ml/sec and can be described by a similar function as in the case of the heights:

$$R_0 = 4.46 \cdot e^{-2.0\,F} \cdot F^{0.5} \tag{12}$$

The ratio of the values of the negative and positive parts of the response were investigated for all three columns during cooling. The ratio increases with increasing flow rate of the gas in all three cases. The dependence for an a-type column is shown in Fig. 6. For b- and d-type columns, the negative part of the response is too small to register at low velocities of the flow of the gaseous mixture, for the b-type column at $F < 0.2$ ml/sec, and for the d-type column at $F < 0.125$ ml/sec.

The dependence of the blank response on the magnitude of the cooled dead volume of the column was measured for all the column types at two flow rates of the gaseous mixture, $F = 0.06$ and 0.250 ml/sec. Empty columns with different radii were used for the measurements. Only positive parts of the responses were studied as negative parts could not be measured in some cases. The value of the radial temperature gradient and the time needed for balancing the temperatures between the column centre and wall increase and, at a constant volume velocity, the linear velocity of the flow of the gaseous mixture also increases with increasing column radius. The value of the blank response will therefore also increase.

The dependence of the blank response on the value of the cooled column volume can be expressed for all the column types during cooling and heating, for the flow rate $F = 0.06$ ml/sec, by means of the following relation:

$$R_0 = m \cdot V_D^q \tag{13}$$

where m and q are constants for a particular column type, with constant flow rate and composition of the gaseous mixture. The values of m and q for all the column types during cooling and heating are shown in Table I. The dependence of the blank response on the column volume at a flow rate of the gaseous mixture $F = 0.250$ ml/sec may be described by the same relation only during column heating. The values of m and q in this case are also shown in Table I. The dependence has another course during column cooling.

The dependence of the blank response on the value of the cooled dead volume, which was changed in that the column was gradually filled with glass tubes, was determined for the column with the capillary inlet of the gaseous mixture in the

TABLE I

THE EFFECT OF COLUMN VOLUME ON THE MAGNITUDE OF BLANK RESPONSE

Values of constants m and q in eqn. 13.

F(ml/sec)	*Tube type*	*Cooling*		*Heating*	
		m	*q*	*m*	*q*
0.06	a	0.165	1.84	0.105	1.45
	b	0.108	0.90	0.155	1.31
	c	0.047	1.46	0.052	1.68
	d	0.014	2.71	0.015	2.60
0.25	a			0.080	4.32
	b			0.031	1.41
	c			0.018	1.23

TABLE II

THE DEPENDENCE OF BLANK RESPONSE ON THE COOLED DEAD VOLUME
Mixture: 22% N_2, 78% H_2, $F = 0.125$ ml/sec.

V_D (ml)	R_{0C} (ml N_2)	R_{0H} (ml N_2)
4.6	0.981	0.840
4.0	0.718	0.612
3.6	0.603	0.406
2.7	0.288	0.201
1.8	0.090	0.057

centre. The response caused by the adsorption of nitrogen on the glass tubes is negligible in comparison with the value of the blank response. Also in this case, the dependence of the blank response on the dead volume of the column can be described by the empirical equation 13. The results for the mixture of 22% (v/v) of nitrogen and 78% (v/v) of hydrogen and $F = 0.125$ ml/sec are listed in Table II. In this case, $m = 0.018$ and $q = 2.6$ during cooling, and $m = 0.011$ and $q = 2.9$ during heating.

In contrast to the case when the column radius changes with the change in the column volume, packing with glass tubes changes neither the value of the radial temperature gradient nor the time necessary for balancing the temperatures between the column wall and centre. However, the profile of the flow in the column is disturbed and the tubes hinder the thermal diffusion. The linear velocity of the mixture of gases increases with decrease in the dead volume of the column at a constant flow rate. The same decrease in the blank response also occurs in the case when the column is packed with the material the surface of which is being measured. The contribution of the blank response to the total response was determined by means of the glass tubes which have a negligible surface area in comparison with that of the material measured.

The dependence of the blank response on the composition of the gases was determined for a tube with the capillary inlet in the centre, dead volume 4.0 ml at a flow rate $F = 0.125$ ml/sec. From Table III it is obvious that the value of the blank response increases, in agreement with the assumptions mentioned previously, with increasing nitrogen concentration in the concentration range which was investigated.

From the results presented, it is obvious that in the cases when columns

TABLE III

THE DEPENDENCE OF THE BLANK RESPONSE ON THE SORBATE CONCENTRATION IN THE GASEOUS MIXTURE
$V_D = 4.0$ ml. $F = 0.125$ ml/sec.

c (% v/v N_2)	R_0 (ml N_2)
20	0.600
24	0.660
27	0.680
30	0.715

with relatively large volumes must be used for the measurements of surface areas by the dynamic desorption method, the contribution of the blank response to the total response measured must not be neglected. The dependence of the blank response on the flow rate of the mixture of gases, the value of the cooled dead volume of the column and the composition of the gaseous mixture, which were found, were used for the selection of suitable conditions for the measurement of small surface areas. The method was used for the measurement of materials which were not powder-like[5,6] (corroded layers on the walls of tubes, pieces of natural and artificial leather, chromatographic paper). The tube with the capillary inlet for the mixture of gases in the centre was used as the measuring column.

The value of the blank response increases with decreasing flow rate of the gaseous mixture, but the ratio of the values of the positive and negative parts of the response increase at the same time. The highest flow rate at which the negative part of the response is not measurable was selected for the measurement. In the investigated range of flow rates, the blank response is lower during column heating than during cooling if the column with the capillary inlet in the centre is used. That is the reason why the desorption curves were selected for the calculations of the surface areas measured.

The size of the column used is affected by the geometry of the material being measured. Measuring columns with relatively large volumes must be used for the measurements described above. The contribution of the blank response would decrease with the use of columns with smaller volumes but at the same time it would be necessary to use smaller samples for the measurements and thus the contribution of the response proportional to the adsorbed volume of nitrogen would also decrease.

The contribution of the blank response and of the response caused by the adsorption also decreases with decrease in nitrogen concentration in the mixture of gases used for the measurement.

REFERENCES

1 R. J. Maggs and T. E. Young, in C. L. A. Harbourn and R. Stock (Editors), *7th International Symposium on Gas Chromatography and its Exploitation*, Copenhagen, 1968.
2 G. H. Thompson, M. N. Myers and J. C. Giddings, *Anal. Chem.*, 41 (1969) 1219.
3 M. E. Hoving, G. H. Thompson and J. C. Giddings, *Anal. Chem.*, 42 (1970) 195.
4 J. C. Giddings, E. M. Hoving and G. H. Thompson, *J. Phys. Chem.*, 74 (1970) 4291.
5 J. Vilím, M. Krejčí and D. Kouřilová, *Chem. Prům.*, in press.
6 M. Krejčí and D. Kouřilová, *Chromatographia*, 4 (1971) 48.
7 E. Cremer and H. Huck, *Glastech. Ber.*, 37 (1964) 511.
8 H. Huck, *Dissertation*, Leopold Franzens Universitat, Innsbruck, 1965.
9 H. Brown, *Phys. Rev.*, 58 (1940) 661.
10 K. E. Grew and T. L. Ibbs, *Thermal Diffusion in Gases*, GITTL, Moscow, 1956, p. 22.
11 J. O. Hirschfelder, Ch. F. Curtis and R. B. Bird, *Molecular Theory of Gases and Liquids*, Izdatel'stvo Innostrannoi Literatury, Moscow, 1961, p. 429.
12 R. B. Bird, W. E. Steward and E. N. Lightfoot, *Transfer Phenomena*, Academia, Prague, 1968, p. 69.
13 R. B. Bird, W. E. Steward and E. N. Lightfoot, *Transfer Phenomena*, Academia, Prague, 1968, p. 66.
14 L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.*, 67 (1945) 1398.
15 E. Whalley, *Trans. Faraday Soc.*, 47 (1951) 815.
16 J. C. Giddings, *Anal. Chem.*, 34 (1962) 722.
17 M. Krejčí and M. Janíček, *Chem. Listy*, 60 (1963) 93.
18 D. Kouřilová and M. Krejčí, *Chem. Listy*, 65 (1971) 742.