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SILICA GEL AND CARBOCHROM B MODIFIED WITH PHTHALOCYANINES AS STATIONARY PHASES IN GAS-SOLID CHROMATOGRAPHY

JÜRGEN HILLE, MIROSLAV PROCHÁZKA, LADISLAV FELTL and EVA SMOLKOVÁ-KEULEMANSOVÁ*

Department of Analytical Chemistry, Charles University, Albertov 2030, 128 40 Prague 2 (Czechoslovakia)
and

A. V. KISELEV, N. V. KOVALEVA and E. V. ZAGOREVSKAYA

Laboratory of Adsorption and Chromatography, Chemical Department, M.V. Lomonosov State University of Moscow, 117234 Moscow (U.S.S.R.)

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SUMMARY

Adsorbents were prepared, based on silica gel modified with phthalocyanine and copper and nickel phthalocyanates (H₂Pc, CuPc, NiPc) by adsorption of phthalocyanine from a solution in concentrated sulphuric acid. Adsorbents based on graphitized thermal carbon black (Carbochroms) were also been prepared. Carbochrom B was modified with copper phthalocyanate using adsorption from 1-bromonaphthalene solution and with sodium salts of the sulphonic acids of copper phthalocyanate [CuPc(SO₃Na)₄] using adsorption from aqueous solutions. Efficient adsorbents, showing high selectivity, were thus obtained. The modified adsorbents were applied to gas-solid chromatographic measurements using packed and micropacked columns. The adsorbates used were *n*-pentane, *n*-hexane, *n*-heptane, cyclohexane, 1-hexene, benzene, diethyl ether, propanol, acetone and nitrobenzene. The advantages of the prepared materials in analytical applications include shorter analysis times, improvement in peak symmetry and separation and high temperature stability. The differential heats of adsorption and the contributions of specific interactions of selected adsorbates were calculated from the chromatographic data and are discussed. The experimental values of the differential heats of adsorption were compared with published data.

INTRODUCTION

Much attention has been paid to adsorbents with chemically modified surfaces. Chemically bonded stationary phases find broad application in both gas and high-performance liquid chromatography^{1,2}. However, adsorbents with modified surfaces can be prepared not only by chemical bonding of the stationary phase to the support surface, but also by physical adsorption. For the latter method substances with planar structures are the most suitable and thus phthalocyanines are advantageous. The modification of adsorbents by phthalocyanine and phthalocyanates has been studied

by several groups³⁻⁷, using silica gel^{3,4} and graphitized thermal carbon black (GTCB)⁵⁻⁷ as the initial material. Phthalocyanine and metal phthalocyanates are soluble in only a few inorganic and organic solvents⁸. Modification of silica gel with phthalocyanine and copper and nickel phthalocyanates by adsorption from a solution in concentrated sulphuric acid and 1-bromonaphthalene and by chemisorption of phthalic acid *o*-dinitrile has been described³. The surface of GTCB was modified^{5,6} by phthalocyanine and copper, cobalt, zinc and nickel phthalocyanates. The solubility of lithium phthalocyanate (Li₂Pc) in ethanol was utilized and the adsorbent surface was coated with this substance. Li₂Pc was then converted into the above phthalocyanates by precipitation with inorganic salts of the metals. Phthalocyanine without the central metal atom (H₂Pc) was obtained by acid hydrolysis with dilute hydrochloric acid. The adsorbents were covered with large amounts of phthalocyanines, greatly exceeding the dense monolayer capacity. Undesirable voluminous crystals of phthalocyanines can then be formed on the adsorbent surface and thus Gavrulina *et al.*⁷ modified the GTCB surface with sodium salts of the sulphonic acids of cobalt phthalocyanates that are soluble in water, using adsorption from aqueous solutions, when no crystals were formed on the adsorbent surface. However, the specific properties of adsorbents modified with sulphonated phthalocyanines depend strongly on the number of sulpho groups in the phthalocyanate molecule.

In this work, previous experience was utilized^{3,7} and Porasil C silica gel was modified with phthalocyanine and with copper and nickel phthalocyanates and the carbonaceous adsorbent Carbochrom B was modified with copper phthalocyanate (CuPc) and with the sodium salts of sulphonic acids of copper phthalocyanate [CuPc(SO₃Na)₄]. The modified and original adsorbents were used under gas-solid chromatographic (GSC) conditions. From the retention data of the adsorbates studied, the molar differential heats of adsorption and the contributions of specific interactions to the adsorption energy were calculated and are discussed.

EXPERIMENTAL

Modification of Porasil C

Phthalocyanines are soluble in a few inorganic and organic solvents⁸. In the introductory experiments, 1-bromonaphthalene was used as a solvent. However, concentrated sulphuric acid has been found to be a much more advantageous solvent^{3,9}. Protonation of the nitrogen atoms of the phthalocyanine skeleton permits much more concentrated phthalocyanine solutions to be obtained. By reversible deprotonation of the cationic form of the dye, the water-insoluble phthalocyanine can be precipitated again. This basic procedure was used for the preparation of modified adsorbents³. During the preparation, great care was observed that all the components used were highly pure.

The initial material for the preparation of the adsorbent was Porasil C silica gel from Waters Assoc. (Milford, MA, U.S.A.), with spherical grains 37-75 μm in diameter, with uniform porosity and a specific surface area of 75 m^2/g . Its surface was modified with phthalocyanine and copper and nickel phthalocyanates from VUOS (Pardubice-Rybitví, Czechoslovakia) and from Bayer (Leverkusen, F.R.G.).

The basic characteristics of the adsorbent (specific surface area and coverage) are given in Table I.

TABLE I
BASIC PROPERTIES OF THE ADSORBENTS AND COLUMNS

Coverage is expressed in terms of % (w/w) and in percentage areas covered by the theoretical dense monolayer.

<i>Adsorbent (column packing)</i>	<i>Specific surface area (m²/g)</i>	<i>Coverage (%)</i>		<i>Packing column weight (g)</i>
		<i>w/w</i>	<i>Surface</i>	
Porasil C	94.4	—	—	0.3764
Porasil C + H ₂ Pc	99.0	—	—	0.4172
Porasil C + CuPc	100.0	3.08	60.0	0.4365
Porasil C + NiPc	99.5	2.44	47.0	0.3692

The specific surface areas of the prepared adsorbents and of the unmodified original silica gel were determined by the method of thermal desorption of nitrogen, using a calibration graph obtained with silica gel standards with surface areas measured by the BET method. The coverage of the modified adsorbents was calculated from the known dimensions of the phthalocyanine molecule and the amount of the dye deposited on the silica gel surface. The coverage of the adsorbent with metal phthalocyanates was determined from the concentration of the central metal ion of the phthalocyanine complexes¹⁰. In 1 ml of concentrated nitric acid, 0.5 g of a modified adsorbent was oxidized, with boiling. The central cation liberated from the phthalocyanate was determined by differential pulse polarography under the following conditions: half-wave potentials, +0.4 and -0.9 V for copper and nickel, respectively; drop time, 1 sec; voltage pulse width, 100 msec; sampling period, 20 msec; and pulse amplitude, 50 mV. The polarographic measurements were carried out on a PA-3 instrument from Laboratorní přístroje (Prague, Czechoslovakia).

The coverage of phthalocyanine-modified silica gel was calculated from the contents of C, H and N obtained from organic elemental analysis.

The prepared adsorbents and the original Porasil C were packed in a glass column 900 mm long and 1 mm I.D. The adsorbates used were API standards (U.S.A.).

The chromatographic measurements were carried out on a Hewlett-Packard 5700A gas chromatograph with a flame-ionization detector. Most experiments were performed at a carrier gas flow-rate of 15–20 ml/min. The measurements were carried out isothermally at seven different temperatures from 100 to 130°C for hydrocarbons and from 160 to 190°C for their derivatives. The adsorbates were injected as saturated vapours at laboratory temperature, in amounts of 1–50 µl, using Hamilton syringes.

Modification of Carbochrom B

The initial adsorbent, Carbochrom B (18% pyrolytically deposited carbon on the surface of GTCB, with a specific surface area of 8 m²/g and a grain size of 0.25–0.50 mm), was described earlier¹¹. It was modified with copper phthalocyanate by adsorption from 1-bromonaphthalene solution, as described elsewhere^{3,12}. The modification of Carbochrom B with the sodium salt of the sulphonic acid of copper phthalocyanate was carried out using the procedure published earlier⁷. The volume

of the monomolecular layer was determined as follows: (a) from the isotherm of the adsorption of $\text{CuPc}(\text{SO}_3\text{Na})_4$ from water on to Carbochrom B at 23°C; (b) from the Van der Waals dimensions of the $\text{CuPc}(\text{SO}_3\text{Na})_4$ molecules arranged in the plane of the Carbochrom B surface; and (c) from the dependence of the retention volumes of various adsorbates on the amount of the modifying substance on the Carbochrom B surface. The three methods yielded analogous results, given in Table II.

The thermal stability of the modified Carbochroms was calculated from the retention volumes of various adsorbates before and after heating the adsorbents for 5 h at various temperatures in a stream of carrier gas at a flow-rate of 30 ml/min. The chromatographic measurements were carried out on a Tsvet-1 chromatograph with a flame ionization detector, using glass columns 500 mm long and of 3 mm I.D. with a nitrogen carrier gas flow-rate of 40 ml/min.

TABLE II
DENSE MONOLAYER CAPACITY OF $\text{CuPc}(\text{SO}_3\text{Na})_4$ ON CARBOCHROM B DETERMINED BY DIFFERENT METHODS

<i>Dense monolayer capacity (m^2/g)</i>		
<i>From isotherm of adsorption from solutions</i>	<i>From GC data</i>	<i>Calculated from Van der Waals dimensions of modifier molecule</i>
0.7 ± 0.1	0.8 ± 0.1	0.66

RESULTS AND DISCUSSION

Determination of the heats of adsorption of the adsorbates

The chromatographic measurements were carried out in the temperature range 100–130°C for the adsorbates *n*-pentane, *n*-hexane, *n*-heptane, 1-hexene, cyclohexane and benzene and in the temperature range 160–190°C for diethyl ether, propanol and nitrobenzene. In each temperature range, the retention characteristics were measured at seven column temperatures and the retention volumes per unit surface area were calculated from the mean adjusted retention times of the adsorbates.

The values of the molar differential heats of adsorption, \bar{q}_1 , for the adsorbates were calculated from the slope of the linear dependence $\log V_s = f(1/T)$, where *T* is the column temperature and V_s is specific retention volume per m^2 of the adsorbent.

The precision of the \bar{q}_1 values was evaluated statistically. The relative error was 0.5–1.0%, and the data obtained can therefore be interpreted with sufficient reliability.

The contributions from specific intermolecular interactions were found by linear regression from the dependence of the molar differential heat of adsorption for *n*-alkanes on the polarizability, α , of their molecules^{1,2}. For the adsorbates *n*-pentane, *n*-hexane and *n*-heptane, the parameters of the linear function $\bar{q}_1 = f(\alpha)$ were determined.

The contribution of the specific interaction of polar adsorbates, $\Delta\bar{q}_{1,\text{spec.}}$, was

found from the difference between \bar{q}_1 for the polar adsorbate and $\Delta\bar{q}_{1,\text{non-spec.}}$. The latter value was calculated by interpolation of the function $\bar{q}_1 = f(\alpha)$ for the appropriate polarizability corresponding to the given polar adsorbate¹².

Porasil C modified with phthalocyanines: adsorbate-adsorbent interaction and comparison of experimental and published data

The experimental values of the molar differential heats of adsorption are summarized in Tables III and IV and the published data for GTCB are given in Table V. The interpretation of the results is based on a comparison of \bar{q}_1 on silica gel with the published values for GTCB⁵. By modification of GTCB with phthalocyanine or with metal phthalocyanates, an adsorbent with specific properties is obtained from the non-specific adsorbent, *i.e.*, an adsorbent of the 1st type is converted into an adsorbent of the 3rd type¹³. The original silica gel and silica gel modified with phthalocyanines both have specific properties; the surface of the unmodified adsorbent exhibits only the effect of the hydroxyl groups. Modification with phthalocyanine or

TABLE III

DIFFERENTIAL HEATS OF ADSORPTION FOR THE ADSORBATES AND THEIR STANDARD DEVIATIONS (\bar{q}_1 , kJ/mol)

Sorbate	Porasil C	Porasil C + H ₂ Pc	Porasil C + CuPc	Porasil C + NiPc
<i>n</i> -Pentane	25.25 ± 0.12	31.76 ± 0.51	30.81 ± 0.25	31.04 ± 0.24
<i>n</i> -Hexane	31.75 ± 0.15	38.64 ± 0.13	35.35 ± 0.14	32.78 ± 0.18
<i>n</i> -Heptane	34.10 ± 0.14	41.43 ± 0.15	39.49 ± 0.13	39.31 ± 0.88
1-Hexene	37.34 ± 0.14	41.33 ± 0.12	41.15 ± 0.12	39.60 ± 0.15
Cyclohexane	30.75 ± 0.17	36.94 ± 0.20	34.29 ± 0.18	33.00 ± 0.20
Benzene	41.76 ± 0.17	44.90 ± 0.12	45.61 ± 0.12	44.35 ± 0.17
Diethyl ether	62.61 ± 0.37	60.63 ± 0.14	53.59 ± 0.29	55.61 ± 0.19
<i>n</i> -Propanol	—	60.37 ± 0.16	60.64 ± 0.15	56.77 ± 1.69
Nitrobenzene	68.07 ± 0.35	65.30 ± 0.15	61.61 ± 0.24	61.59 ± 0.18

TABLE IV

SPECIFIC CONTRIBUTIONS, $\bar{q}_{1,\text{spec.}}$, TO THE OVERALL MOLAR DIFFERENTIAL HEAT OF ADSORPTION, \bar{q}_1 (kJ/mol)

Upper values, \bar{q}_1 ; lower values, $\Delta\bar{q}_{1,\text{non-spec.}} + \Delta\bar{q}_{1,\text{spec.}}$ ($\bar{q}_1 = \Delta\bar{q}_{1,\text{non-spec.}} + \Delta\bar{q}_{1,\text{spec.}}$).

Sorbate	Porasil C	Porasil C + H ₂ Pc	Porasil C + CuPc	Porasil C + NiPc
Cyclohexane	30.7	36.9	34.3	33.0
	28.2 + 2.5	35.0 + 2.0	33.1 + 1.2	32.4 + 0.6
Benzene	41.8	44.9	45.6	44.3
	26.8 + 14.9	33.4 + 11.5	31.8 + 13.9	31.1 + 13.3
Diethyl ether	62.6	60.6	53.6	55.6
	23.7 + 38.9	30.0 + 30.6	28.7 + 24.9	28.1 + 27.5
<i>n</i> -Propanol	—	60.4	60.6	56.8
	18.5	24.4 + 36.0	23.6 + 37.0	23.3 + 33.4
Nitrobenzene	68.1	65.3	61.6	61.6
	33.1 + 34.9	40.3 + 25.0	37.9 + 23.7	37.0 + 24.6

TABLE V

COMPARISON OF MOLAR DIFFERENTIAL HEATS OF ADSORPTION ON SILICA GEL AND GTCB (\bar{q}_1 , kJ/mol)

The upper values relate to silica gel and the lower values to GTCB.

<i>Sorbate</i>	<i>Unmodified adsorbents</i>	<i>Adsorbents modified with H₂Pc</i>	<i>Adsorbents modified with CuPc</i>	<i>Adsorbents modified with NiPc</i>
<i>n</i> -Pentane	25.8	31.8	30.8	31.0
	37.3	28.9	31.4	32.7
<i>n</i> -Hexane	31.8	38.6	35.4	32.8
	43.5	34.3	36.8	38.1
<i>n</i> -Heptane	34.2	41.4	39.5	39.3
	52.3	39.8	41.4	42.3
Cyclohexane	30.7	36.9	34.3	33.0
	36.4	30.1	30.6	33.5
Benzene	41.8	44.9	45.6	44.3
	41.0	34.8	42.3	38.1
Diethyl ether	62.6	60.6	53.6	55.6
	36.8	28.5	31.4	45.2

a phthalocyanate yields a sorbent containing π -bonds on the surface, *i.e.* an adsorbent of the 3rd type is formed from an adsorbent of the 2nd type.

Interactions of alkanes. The modification of silica gel widens the possibilities of non-specific intermolecular interactions; therefore, the molar differential heats of adsorption increase (Table III). Alkanes can react with the organic skeleton of phthalocyanine, presumably through dispersion forces. Even better conditions for non-specific interactions are provided by GTCB owing to its non-polar surface. This can best be evaluated considering the relatively large energy contributions from CH₂ groups in the homologous series of *n*-alkanes. On modification of GTCB with phthalocyanines, the \bar{q}_1 values approach those obtained on modified silica gel. The highest interaction energies for alkanes are obtained on silica gel modified with phthalocyanine.

Interaction of 1-hexene. The intermolecular interaction energy of 1-hexene is higher than that of hexane on the original silica gel, owing to the presence of the double bond, which permits specific interactions with the hydroxyl groups of silica gel (see Table III). On the modified adsorbents, the interaction energies, \bar{q}_1 , increase, similarly to those of alkanes, which can be explained by possible non-specific intermolecular interactions with the organic skeleton of phthalocyanine or phthalocyanates. Whereas the interaction energy is lower on the adsorbents modified by metal phthalocyanates, the energy for hexene remains constant for all the modified adsorbents, possibly because of a contribution from a specific interaction of the 1-hexene π -bond with the central cations.

Interaction of cyclohexane. The same effect as with alkanes was observed with cyclohexane; the modification leads to an increase in the interaction energy, \bar{q}_1 , on silica gel and to a decrease on GTCB, which again can be explained by non-specific interactions. The interaction energy of cyclohexane is comparable to that of hexane

(see Table IV); the higher value for hexane can be explained by differences in the stereochemical arrangements and polarizabilities of the two molecules.

Interaction of benzene. Benzene is polar but the polarizabilities of benzene and cyclohexane are comparable. The greater interaction energy here is caused by the π -electron system of benzene. The interaction energies on unmodified silica gel and GTCB are comparable, but the adsorption forces have different natures. The π -electrons of benzene induce dipoles on the GTCB surface and the dipoles then interact with the π -electron sextet; on silica gel, the π -electron sextet interacts much more strongly with the surface hydroxyl groups.

The modification of GTCB leads to a decrease in the interaction energy (see Table V), which may be caused by repulsion between the π -electrons of benzene and those of phthalocyanine. If the phthalocyanine skeleton contains a central cation, the \bar{q}_1 values increase, probably owing to interaction of the π -electrons with this cation. In addition, the surface concentration of the force centres of the modifier is smaller than the surface concentration of the original adsorbents^{12,13}. On modified silica gels, the total interaction energies are higher than on the unmodified adsorbent and their values are similar (see Table III).

The separation of the interaction energy into non-specific and specific contributions (see Table IV) gives a deeper insight into the principle of the total interaction. The largest specific contribution to the total interaction energy is found with the original silica gel and is given by the surface hydroxyl groups. Adsorbents modified with metal phthalocyanates exhibit smaller specific contributions to the total value of \bar{q}_1 . If there is no central cation present on the phthalocyanine-modified adsorbent, the specific contribution to the total interaction energy decreases further, which confirms the effect of the central cation on the interaction of the π -electron sextet with the phthalocyanate molecules.

Interaction of adsorbates containing heteroatoms. Diethyl ether has a dipole moment lower than that of propanol, but its polarizability is higher, owing to different bonding of the oxygen atom. Therefore, specific contributions to the total interaction energy predominate with the more polar propanol (see Table IV). With the less polar diethyl ether, this part of the interaction energy is greater than the non-specific part on silica gel. On the modified adsorbents, the specific and non-specific parts are the same. The hydroxyl groups of Porasil C yield better conditions for the hydrogen bonding and, in turn, the organic skeleton shields this effect, leading to a decrease in the intensity of specific interactions and an increase in non-specific contributions, which is presumably due to dispersion interactions with the phthalocyanine organic skeleton. The smaller \bar{q}_1 values for the adsorbents modified by metal phthalocyanates (see Tables III and IV) can be explained by interaction of acidic hydrogen atoms of free phthalocyanine, which permits hydrogen bonding.

Accurate values of the molar differential heats of adsorption could not be obtained for propanol because of its strong tailing on the original Porasil C and on that modified with phthalocyanine. However, it can be seen from Table IV that specific interactions are greater than non-specific interactions. The non-specific part of the total energy is also smaller than on the modified adsorbents. The assumed greater interaction energy confirms a greater specific contribution of the interaction on the original silica gel, owing to hydrogen bonding.

Nitrobenzene has the highest dipole moment of all the adsorbates and exhibits

the greatest \bar{q}_1 value on the original adsorbent, which can again be explained by specific interactions (see Tables III and IV). On the modified adsorbents the ratio between the specific and non-specific contributions in the intermolecular interaction energy is shifted in favour of the latter, owing to an interaction of the phthalocyanine organic skeleton. On comparison of the \bar{q}_1 values on the modified adsorbents, the highest value on the phthalocyanine-modified silica gel can again be explained by hydrogen bonding between acidic hydrogen atoms of phthalocyanine and the oxygen atoms of nitrobenzene.

Sum of interaction energies. The modification of silica gel (Porasil C) by phthalocyanine or a metal phthalocyanate leads to conversion of a 2nd type adsorbent into a 3rd type adsorbent¹³. Specific interactions cause the adsorption on unmodified silica gel. The silica gel surface hydroxyl groups can interact either through hydrogen bonding with the double-bond π -electrons, electrostatic orientation, or through dipoles induced in non-polar adsorbates.

On the modified adsorbents, non-specific interaction of the adsorbates with the organic skeleton of phthalocyanine or phthalocyanates play a role. The acidic hydrogen atoms of phthalocyanine permit hydrogen bonding with adsorbates containing a heteroatom. The central metal cations of phthalocyanates have an effect on the interaction with the π -electron sextet of the benzene rings of the adsorbate.

Carbochrom B modified with phthalocyanine — gas chromatographic properties of the adsorbents

The retention volumes, $V_{A,1}$, and the relative retentions for various adsorbates on original and modified Carbochroms are given in Tables VI and VII, respectively. It can be seen from Table VI that the retention volumes of *n*-alkanes on a monomolecular layer of $\text{CuPc}(\text{SO}_3\text{Na})_4$ are lower than those on the original Carbochrom, which is in agreement with a decrease in the concentration of force centres on the surface of the modified adsorbent. The retentions of ethers, ketones and especially alcohols rapidly increase on the modified adsorbents, indicating strong specific interactions of these adsorbates with the $\text{CuPc}(\text{SO}_3\text{Na})_4$ molecules on the Carbochrom surface.

On Carbochrom B modified with copper phthalocyanate, the $V_{A,1}$ value is even more decreased for *n*-alkanes, whereas the change is less for substances whose molecules cannot specifically interact with the molecules of the modifying substance.

TABLE VI
RETENTION VOLUMES ON THE ORIGINAL AND MODIFIED CARBOCHROM B AT 120°C
(ml/g)

<i>Adsorbent</i>	<i>n-Hexane</i>	<i>n-Heptane</i>	<i>Benzene</i>	<i>Acetone</i>	<i>Diethyl ether</i>	<i>n-Propanol</i>
Carbochrom B	16.0	56.0	10.0	1.4	3.5	2.2
Carbochrom B + 0.6 mg/m ² CuPc	2.0	5.8	2.1	2.7	1.1	1.9
Carbochrom B + 0.8 mg/m ² CuPc(SO ₃ Na) ₄	7.2	24.1	8.8	10.4	6.2	21.3

TABLE VII

RELATIVE RETENTIONS TO *n*-HEXANE ON THE ORIGINAL AND MODIFIED CARBOCHROM B

Adsorbent	<i>n</i> -Hexane	<i>n</i> -Heptane	Benzene	Acetone	Diethyl ether	<i>n</i> -Propanol
Carbochrom B	1.0	3.6	0.62	0.09	0.22	0.14
Carbochrom B + 0.6 mg/m ² CuPc	1.0	2.9	1.1	0.85	0.55	0.68
Carbochrom B + 0.8 mg/m ² CuPc(SO ₃ Na) ₄	1.0	3.3	1.2	1.40	0.86	2.90

To exclude the effect of the specific surface area and to emphasize the role of specific interactions, relative retentions for some adsorbates on the original and modified Carbochrom B are given in Table VII. For *n*-alkanes, the values are similar on all the adsorbents; the relative retentions are substantially higher on the modified sorbent for adsorbates whose molecules can specifically interact with the molecules of the modifying substance.

As can be seen from Table VIII, the \bar{q}_1 values for *n*-alkanes that characterize the ability of the adsorbent to interact non-specifically are similar for the modified and unmodified adsorbent.

For substances whose molecules can interact specifically with the functional groups of the molecules of the modifying substance, the \bar{q}_1 values increase with increasing amount of the modifying substance on the Carbochrom B surface.

The contribution of specific interactions, $\bar{q}_{1,\text{spec.}}$, differs for various adsorbates. According to Kiselev's classification¹³ for substances of group B, *i.e.*, benzene, diethyl ether and acetone, the contribution of specific interactions is about 10–15% of the total adsorption energy, and for substances of group D, *i.e.*, alcohols, it even exceeds 50%. On the modification of Carbochrom B with copper phthalocyanate, this contribution is smaller for all adsorbates than that on the modification with CuPc(SO₃Na)₄. It can be seen that the specific properties of the modified Carbochrom B are caused primarily by the presence of the -SO₃Na groups in the molecules of the modifying substance.

These results are in agreement with those obtained by Gavrilina *et al.*⁷, who modified GTCB with sodium salts of sulphonic acids of cobalts phthalocyanate. The energy of the specific interactions of substances of groups B and D slowly increases with increasing number of sulphonic groups in the phthalocyanate molecule. The effect of the central cation in the molecule of a sulphonated phthalocyanate is substantially smaller than with unsulphonated metal phthalocyanates⁵.

Practical application of the modified adsorbents in GCS analysis

The prepared sorbents were used as stationary phases in glass micropacked and packed columns. The partially modified silica gel sorbents can be used to advantage in analyses of mixtures of alkanes, arenes and various polar substances. However, optimal separations of mixtures of nitrogen-containing substances were achieved only with totally covered adsorbents. Isobutylamine and *n*-pentylamine were separated satisfactorily in a relatively short time at 200 and 250°C on Porasil C

TABLE VIII
 HEATS OF ADSORPTION, \bar{q}_1 , AND CONTRIBUTIONS OF SPECIFIC INTERACTION ENERGY, $\Delta\bar{q}_{1,spec.}$, IN ADSORPTION ON CARBOCHROM
 B MODIFIED BY VARIOUS AMOUNTS OF $\text{CuPe}(\text{SO}_3\text{Na})_4$ AND CuPe (kJ/mol)

Adsorbate	Original Carbochrom B		$\text{CuPe}(\text{SO}_3\text{Na})_4$ (% , v/w)				0.6 mg/m ² CuPe	
	\bar{q}_1		0.2		0.4		0.6	
	\bar{q}_1	$\Delta\bar{q}_{1,spec.}$	\bar{q}_1	$\Delta\bar{q}_{1,spec.}$	\bar{q}_1	$\Delta\bar{q}_{1,spec.}$	\bar{q}_1	$\Delta\bar{q}_{1,spec.}$
<i>n</i> -Pentane	41.4	—	40.5	—	43.1	—	43.5	—
<i>n</i> -Hexane	47.2	—	45.6	—	49.3	—	49.7	—
<i>n</i> -Heptane	53.1	—	51.4	—	54.3	—	54.8	—
<i>n</i> -Octane	58.9	—	57.3	—	60.2	—	60.6	—
Benzene	44.7	—	44.3	2.5	47.2	2.9	50.2	5.8
Acetone	33.0	—	45.1	15.5	50.5	17.6	53.1	20.5
Diethyl ether	42.2	—	48.1	7.9	52.3	9.6	59.8	16.3
<i>n</i> -Propanol	33.8	—	55.6	32.0	—	—	—	—
							47.5	20.2

modified with nickel phthalocyanate (Fig. 1a). The components were not separated on the unmodified adsorbent even at 200°C and the peak exhibited considerable tailing (Fig. 1b).

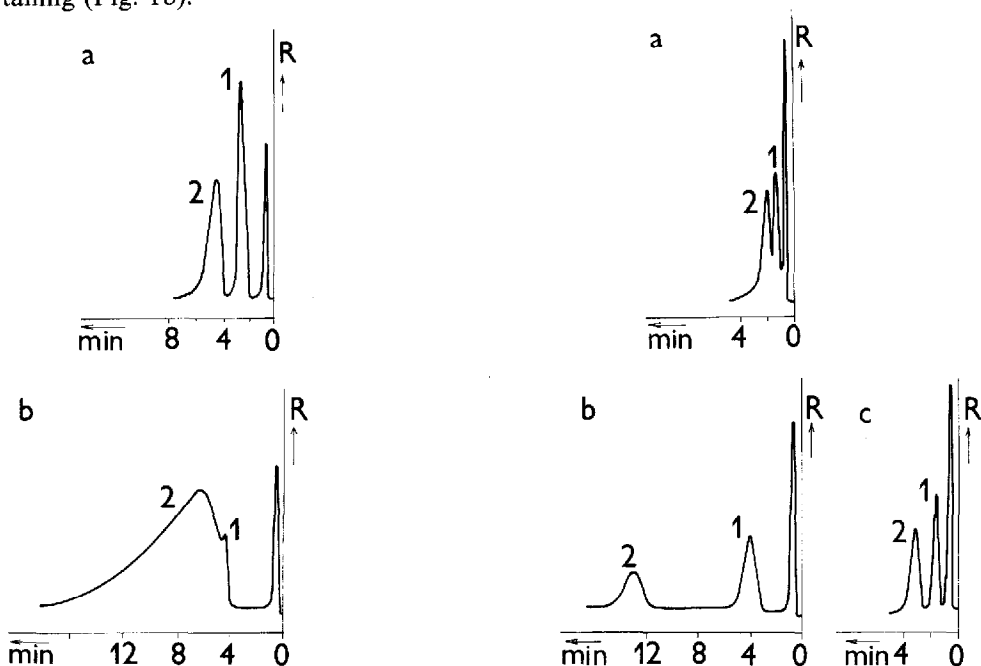


Fig. 1. Separation of a mixture of aliphatic amines: 1 = isobutylamine; 2 = *n*-pentylamine. Micropacked columns (295 × 1 mm I.D.); temperature, 200°C. (a) Porasil C modified with nickel phthalocyanate; linear velocity $u = 15.1$ mm/sec; (b) Porasil C, $u = 22.7$ mm/sec. R is response in mV.

Fig. 2. Separation of a mixture of aromatic amines: 1 = aniline; 2 = *N,N*-dimethylaniline. Micropacked columns (295 × 1 mm I.D.). (a) Porasil C, 220°C, $u = 20.3$ mm/sec; (b) Porasil C modified with phthalocyanine, 220°C; (c) Porasil C modified with phthalocyanine, 250°C.

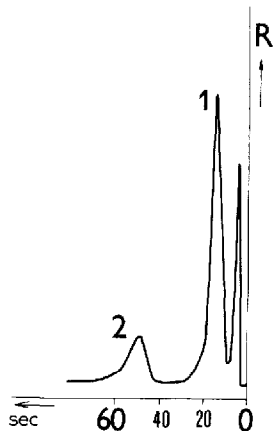


Fig. 3. Separation of a mixture of aromatic amines: 1 = aniline; 2 = *N,N*-dimethylaniline. Micropacked columns (295 × 1 mm I.D.); temperature, 200°C. Porasil C modified with copper phthalocyanate, $u = 73.8$ mm/sec.

Aniline and N,N-dimethylaniline were partially separated on silica gel at 230°C; their separation improved on decreasing the temperature to 220°C (Fig. 2a), but a much better separation was achieved under the same conditions on a column packed with Porasil C modified with free phthalocyanine without a central metal atom (Fig. 2b). The time of analysis can be reduced almost 6-fold by increasing the temperature to 250°C, good resolution of the components being retained (Fig. 2c).

A similar separation of aromatic amines was obtained on adsorbents modified with copper and nickel phthalocyanates; with silica gel modified with copper phthalocyanate the analysis was complete within less than 60 sec (Fig. 3).

It should be emphasized that these separations were carried out successfully on micropacked columns less than 30 cm long. The positive effect of specific interactions of phthalocyanine was especially marked in the analysis of a mixture of aniline and N,N-dimethylaniline, where the two components were completely separated owing to the specificity of the modified adsorbent (Fig. 2b and c). Because of the use of micropacked columns, the time of analysis was substantially shorter than that in the work of Vidal-Madjar⁵. The separation of aromatic amines took less than 60 sec, retaining good separation efficiency (Fig. 3), *i.e.*, the analysis time was 20 times shorter with only a 4-fold increase in the linear flow-rate.

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