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SILICA GEL MODIFIED WITH PHTHALOCYANINES AS A STATIONARY PHASE IN GAS-SOLID CHROMATOGRAPHY

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SUMMARY

Sorbents have been prepared based on silica gel modified with phthalocyanine and with copper and nickel phthalocyanates. The modification was carried out by adsorbing phthalocyanines from solution and by chemisorbing the *o*-phthalodinitrile on silica gel. Effective sorbents have thus been obtained with high selectivity, especially for separations of nitrogen-containing substances. The modified sorbents have been used in micropacked columns in gas-solid chromatography. *n*-Alkanes, arenes, six-carbon substances of various polarities, alcohols and nitrogen-containing substances were used as sorbates. The advantages of sorbents include a reduction in analysis time, an improvement in peak symmetry, the separation of components of mixtures and the high thermal stability of phthalocyanines.

INTRODUCTION

Silica gel has been used in many chromatographic techniques, as the support for the stationary phase in gas-liquid chromatography or as a sorbent in gas-solid (GSC), thin-layer, high-performance liquid and ion-exchange chromatography, either in its original form or variously modified^{1,2}. The sorption properties of silica gel can be suitably modified by thermal and hydrothermal treatment³⁻⁶ or by chemical modification of its surface, for which a number of substances have been used. The reactivity of the hydroxyl groups in silica gel allows the bonding of a wide variety of organic radicals to the surface, thus giving a large selection of sorbents that are used extensively in both gas and high-performance liquid chromatography⁷⁻¹⁰.

However, sorbents with chemically modified surfaces can also be prepared by employing physical adsorption. Substances with planar molecules are most suitable for this purpose and therefore phthalocyanines (Fig. 1) are also advantageous.

Modification of sorbents with phthalocyanines has been systematically studied by Vidal-Madjar¹¹ and Vidal-Madjar and Guiochon¹², who adsorbed phthalocyanines on a non-specific, non-polar type of sorbent, thermally graphitized carbon black

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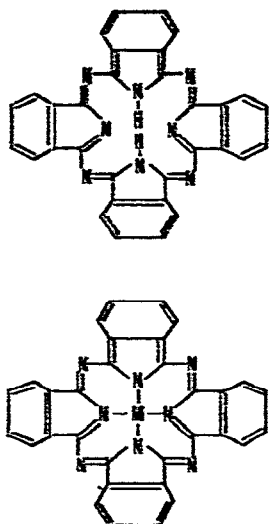


Fig. 1. Molecules of phthalocyanine ($C_{32}N_8H_{16}$) and a metal phthalocyanate ($C_{32}N_8H_{16}M$).

(TGCB). This paper describes the preparation and use of silica gel modified with phthalocyanine and copper and nickel phthalocyanates.

n-Alkanes (pentane to tridecane), arenes (benzene, toluene to butylbenzene), six-carbon ketones and esters and alcohols (methanol to pentanol) were used as sorbates¹³. From the analytical point of view, the separations of nitrogen-containing substances described here appear especially interesting.

EXPERIMENTAL

As the starting material for the preparation of the sorbents, chemically pure Porasil C silica gel (Waters Assoc., Milford, Mass., U.S.A.) was used, with spherical particles 37–75 μm in diameter and with a uniform porosity, the specific surface area being 75 m^2/g . Various procedures were employed for surface modification. Phthalocyanine and copper and nickel phthalocyanates (Research Institute for Organic Syntheses, Pardubice, Czechoslovakia and Bayer, Leverkusen, G.F.R.) were used. The prepared sorbents were packed in glass micropacked columns (295 \times 1 mm I.D.). The sorbates used were API standards.

Chromatographic measurements were performed on a Hewlett-Packard 5700A gas chromatograph equipped with a flame-ionization detector. Nitrogen was used as the carrier gas. Most experiments were carried out at linear flow-rates from 15 to 22 mm/sec , isothermally over a temperature range of 100–250°. The sorbates were injected in the form of saturated vapours at laboratory temperature in amounts of 1–50 μl using Hamilton syringes.

RESULTS AND DISCUSSION

Methods of modification of silica gel with phthalocyanines

Silica gel was modified with phthalocyanines by adsorption from solution and

by chemisorption of *o*-phthalodinitrile. Phthalocyanines are soluble in only a few inorganic and organic solvents¹⁴. In initial experiments 1-bromonaphthalene was used as the solvent. However, concentrated sulphuric acid was found to be much better as protonation of the nitrogen atoms of the phthalocyanine skeleton makes it possible to prepare sufficiently concentrated phthalocyanine solutions. By reversible deprotonation of the cationic form of the dye produced, the water-insoluble phthalocyanine can again be precipitated. This basic procedure was used in the preparation of the modified sorbents. High purity of all reagents was maintained throughout the preparation.

Sorption from 1-bromonaphthalene solution. For the preparation of a modified sorbent, the solubility of phthalocyanine in 1-bromonaphthalene at an elevated temperature was utilized. The solvent was purified by distillation *in vacuo* at 200° on a 50-cm silica gel column.

Saturated solutions of phthalocyanine in 1-bromonaphthalene were prepared at 250° in a flask fitted with a reflux condenser.

Phthalocyanine was adsorbed on the surface of silica gel by mixing freshly activated silica gel with hot, filtered, saturated solutions of phthalocyanine and copper phthalocyanate in 1-bromonaphthalene. The dye solutions were added in one batch. After 24 h the mixture was filtered and the silica gel was washed with methanol and *n*-heptane and dried *in vacuo* at 150–200°.

Sorption from concentrated sulphuric acid solution. In contrast with the previous procedure, yielding sorbents with a low surface coverage (27 and 41 %), this method produces sorbents with a totally covered surface.

A number of variously modified sorbents was prepared and the surface coverage was determined (see below). From the dependence of the surface coverage on the equilibrium phthalocyanine concentration in sulphuric acid, the optimal concentration of the phthalocyanine solution for the preparation of sorbents with completely modified surfaces was found.

An amount of 0.5 g of phthalocyanine or metal phthalocyanate was dissolved in 5 ml of concentrated sulphuric acid at 70°, under a nitrogen atmosphere and with constant stirring, to prevent oxidation of the phthalocyanine skeleton. Immediately after complete dissolution of the dye, 1 g of silica gel was added to the solution. After cooling of the mixture, the silica gel was isolated and contained the protonated form of phthalocyanine on the surface. Deprotonation was achieved by hydrolysis in a large excess of boiling water (1000 ml) with vigorous stirring. The sedimented modified sorbent was then filtered off on a frit.

In addition to the adsorbed phthalocyanine, the sorbent surface contains a certain amount of mechanically trapped dye, because of the use of concentrated solutions. The excess of dye was separated using the hydrophobicity of phthalocyanines and their insolubility in water, by ultrasonic treatment of the sorbent particles dispersed in water. Excess of dye was removed by a water pump. The sorbent was then dried and activated *in vacuo* at 150–200°.

Phthalocyanine formed from o-phthalodinitrile. The modification of silica gel by chemisorption *o*-phthalodinitrile was also tested.

Silica gel was heated with excess *o*-phthalodinitrile in an electric oven at 390°. The blue-green reaction mixture formed was placed in excess of chloroform (250 ml), in which the dinitrile is readily soluble. The modified silica gel was freed of excess of

unreacted *o*-phthalodinitrile by repeated extraction with chloroform and then dried and activated *in vacuo* at 150–200°.

The dye formed was identified spectrophotometrically in the UV and visible regions (Fig. 2), after extracting the dye formed from 5 g of modified silica gel with sulphuric acid.

The absorption spectrum of the synthesized dye (curve 1) is different from curve 3, corresponding to the initial reactant, confirming that the modified sorbent was sufficiently purified by the extraction from unreacted *o*-phthalodinitrile.

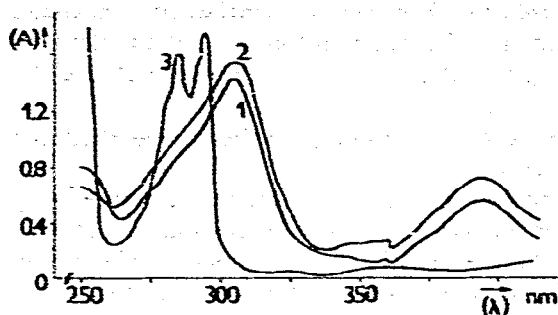


Fig. 2. Absorption spectra of substances dissolved in sulphuric acid: 1 = synthesized dye; 2 = phthalocyanine; 3 = *o*-phthalodinitrile.

However, the agreement of the absorption maxima of curves 1 and 2 is not unambiguous proof of the presence of the phthalocyanine skeleton on the silicagel surface. Therefore, several milligrams of the synthesized dye were isolated by the hydrolytic method and subjected to mass spectrometric analysis. At an ionization energy of 75 eV and an accelerating voltage of 8 kV the existence of a molecular ion with *m/e* 514, corresponding to phthalocyanine without a central metal atom, was confirmed at 375°.

By chemisorption of *o*-phthalodinitrile, silica gel modified with phthalocyanine was prepared with an average surface coverage of 26%.

Application of the modified sorbents in GSC

The prepared sorbents were used as stationary phases in glass micropacked columns. The surface coverage was found by organic elemental analysis and spectrophotometry, the specific surface area was determined by the thermal desorption method and thus the principal characteristics of the sorbents were obtained (see Table I).

The partially modified 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 sorbents.

Isobutylamine and *n*-pentylamine were separated satisfactorily in a relatively short time at 200 and 250° on Porasil C modified with nickel phthalocyanate (Fig. 3a). The components were not separated on the unmodified sorbent even at 200° and the peak exhibited considerable tailing (Fig. 3b).

TABLE I
PROPERTIES OF THE ADSORBENTS

Adsorbent	Specific surface area (m^2/g)	Surface coverage (%, w/w)*
Phthalocyanine-modified silica gel	123	9.1
Copper phthalocyanate-modified silica gel	111	23.0
Nickel phthalocyanate-modified silica gel	214	40.2
Silica gel	75	—

* The percentages (w/w) of the modifying substance corresponding to the total coverage of the sorbent surface are as follows: for silica gel + $C_{32}N_8H_{18}$, 3.790%; for silica gel + $C_{32}N_8H_{16}Cu$, 4.207%; and for silica gel + $C_{32}N_8H_{16}Ni$, 4.213%.

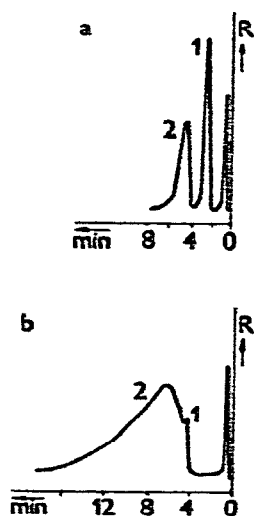


Fig. 3. Separation of a mixture of aliphatic amines: 1 = isobutylamine; 2 = *n*-pentylamine. Micro-packed columns (295×1 mm I.D.); temperature, 200° . (a) Porasil C modified with nickel phthalocyanate, $u = 15.1$ mm/sec; (b) Porasil C, $u = 22.7$ mm/sec.

Aniline and *N,N*-dimethylaniline were partially separated on silica gel at 230° ; their separation improved on decreasing the temperature to 220° (Fig. 4a), 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. 4b). The time of analysis can be reduced almost 6-fold by increasing the temperature to 250° , good resolution of the components being retained (Fig. 4c). A similar separation of aromatic amines was obtained on sorbents modified with copper and nickel phthalocyanates; with silica gel modified with copper phthalocyanate the analysis was completed within less than 60 sec (Fig. 5). It should be emphasized that these separations were carried out successfully on micropacked columns less than 30 cm long.

On comparison of the results obtained with the modified silica gel with those obtained on modified TGCB, it can be seen that in both instances the modification caused a change in the sorbate-sorbent interaction and hence also a change in the sorption properties of the materials. Non-specific TGCB was converted into a sorbent

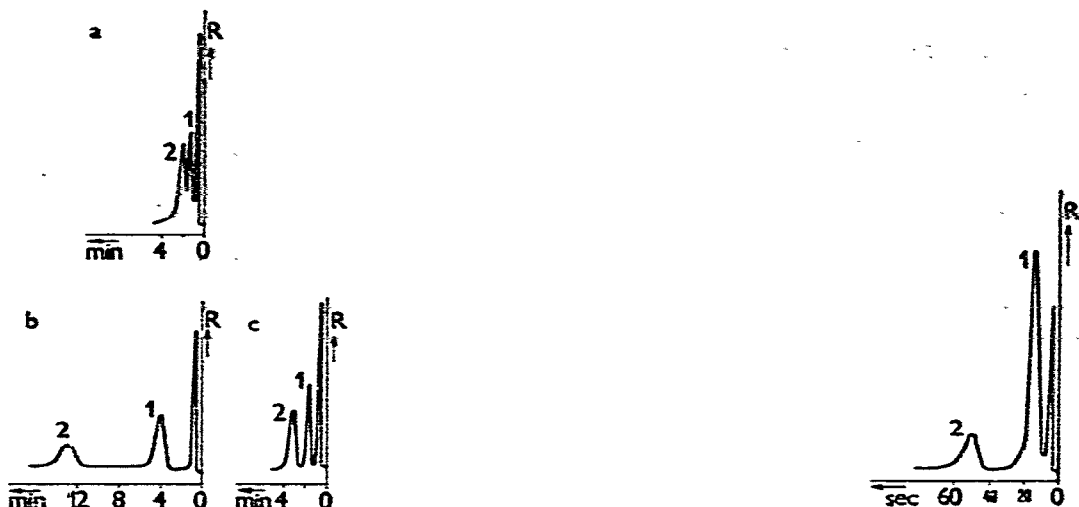


Fig. 4. Separation of a mixture of aromatic amines: 1 = aniline; 2 = *N,N*-dimethylaniline. Micro-packed columns (295×1 mm I.D.). (a) Porasil C, 220° , $u = 20.3$ mm/sec; (b) Porasil C modified with phthalocyanine, 220° ; (c) Porasil C modified with phthalocyanine, 250° .

Fig. 5. Separation of a mixture of aromatic amines: 1 = aniline; 2 = *N,N*-dimethylaniline. Micro-packed columns (295×1 mm I.D.); temperature, 200° . Porasil C modified with copper phthalocyanate, $u = 73.8$ mm/sec.

that allowed specific interactions, resulting in a change in the order of elution of the components of the mixture¹¹.

Silica gel is a specific sorbent with a much more heterogeneous surface than TGCB. However, good agreement was attained in separations of arenes and nitrogen-containing substances on the two sorbents. Modification of the silica gel with phthalocyanines led to especially good results in analyses of mixtures of nitrogen-containing substances (see Figs. 3–5). It also follows from Fig. 3a and b that the modification produced a totally covered sorbent surface, eliminating the negative effect of the hydroxyl groups, which is manifested in non-symmetry of polar sorbate peaks.

The positive effect of specific interactions of phthalocyanines 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 sorbent (Fig. 4a and b).

Because of the use of micropacked columns, the time of analysis was substantially shortened compared with the work of Vidal-Madjar¹². The separation of aromatic amines took less than 60 sec, retaining good separation efficiency (see Fig. 5), *i.e.*, the analysis time was shortened 20-fold with only a 4-fold increase in the linear flow-rate.

Vetrova *et al.*¹⁵ also used silica gel (Silochrom-80) modified with phthalocyanine and metal phthalocyanates and obtained the best results with a sorbent modified with copper chlorophthalocyanate. However, this material is thermally unstable and can be used only up to 130° , whereas our materials yield reproducible results even at temperatures up to 250° . Vetrova *et al.* found that polar substances

are eluted from sorbents modified with copper and zinc phthalocyanates with non-symmetrical peaks and long retention times. These negative effects were attributed to impurities in the initial material. We consider that the good results obtained in the present work are due not only to the use of Porasil C, which is a chemically pure material, but also because sorbents with a totally covered surface were prepared, thus eliminating the negative effect of the hydroxyl groups.

Further possibilities of using phthalocyanines

Planar phthalocyanine molecules could be used for separation of geometric isomers, could widen the range of mobile phases used in high-performance liquid chromatography and could probably find some use in ion-exchange chromatography. These possibilities and the interpretation of the sorbate-sorbent interaction mechanism are being studied.

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