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Facile chemical hydrophobization of thin-layer plates by vapor deposition of methyltrimethoxysilane for reversed-phase chromatography

Julien Jaxel^{1,2} · Alice Merio¹ · Nadine Kohlhuber¹ · Marco Beaumont¹ · Rupert Wimmer³ · Thomas Rosenau^{1,4} · Christian Hansmann^{2,3} · Falk Liebner^{1,5} · Stefan Böhmendorfer¹

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Abstract

Reversed-phase chromatography is based on a polar mobile phase and an apolar stationary phase. This separation mode is regularly used in planar (thin-layer) chromatography, and the necessary plates are commercially available. We investigated the preparation of hydrophobic plates for thin-layer chromatography by chemical vapor sorption of methyltrimethoxysilane directly onto a normal-phase plate. For this, a commercial normal-phase plate is simply exposed to the vapors of the reagent in a closed vessel. The obtained plates were characterized by infrared spectroscopy and dynamic water vapor sorption, which reported an extensive conversion of free hydroxyl groups by the reagent. The obtained plates were hydrophobic with a water contact angle close to 135°. The extent of hydrophobization precluded the use of pure water as an eluent while mixtures with organic solvents were perfectly adequate. The plates' chromatographic performance was compared with that of C18 and paraffin-coated plates. For this, a set of parabens was separated with mixtures of acetone and water. The height of a theoretical plate was similar for the hydrophobized and the C18 plates (50–90 μm) and larger for the paraffin-coated ones. In contrast to the C18 plate, the hydrophobized and the paraffin-coated plates showed some selectivity for the analyte pair *n*-butylparaben and *iso*-butylparaben, which indicates a separation mechanism with the potential for regioselectivity.

Keywords Dynamic vapor sorption · Infrared spectroscopy · Planar chromatography · Organosilane · Paraben · Thin-layer chromatography · Wettability

✉ Stefan Böhmendorfer
stefan.boehmendorfer@boku.ac.at

- 1 Department of Chemistry, Institute of Chemistry of Renewable Resources, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad Lorenz Straße 24, 3430 Tulln an der Donau, Austria
- 2 Wood K Plus – Competence Center for Wood Composites & Wood Chemistry, Kompetenzzentrum Holz GmbH, Altenberger Straße 69, 4040 Linz, Austria
- 3 Department of Material Sciences and Process Engineering, Institute of Wood Technology and Renewable Materials, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad Lorenz Straße 24, 3430 Tulln an der Donau, Austria
- 4 Faculty of Science and Engineering, Laboratory of Natural Materials Technology, Åbo Akademi University, Porthansgatan 3, 20500 Turku, Finland
- 5 Department of Chemistry and CICECO Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

1 Introduction

In thin-layer chromatography (TLC), and its high-performance counterpart (HPTLC), separations are performed most commonly in normal-phase (NP) mode: the stationary phase is hydrophilic, often silica particles immobilized with a binder, and the mobile phase is an apolar solvent. However, in certain cases, for example the separation of parabens [1–4], hormones [5], lipids [6], or drugs [7, 8], a reversed-phase (RP) setup is required for a satisfactory separation. Here, a hydrophobic stationary phase and a hydrophilic mobile phase are used. Advantages of reversed-phase systems are the less hazardous eluents (mixtures of water with acetone, methanol, *et cetera*) and an improved separation efficiency for some more polar compounds [9–11]. Commercially, hydrophobic silica is manufactured by a wet-chemical modification of the polar silica to cover it with *n*-alkyl siloxanes, with alkyl chains that typically have 2, 8, or 18 carbon atoms. Alternatively, hydrophobization of NP

plates can be achieved by physical coating. Previous protocols designed for laboratory experiments described the elution of paraffin oils prior to use [8, 12]. Also, the simple impregnation of NP silica gel plates with paraffin solutions yields a hydrophobic coating of the silica particles' surface and the porous network of the particle bed. The effectiveness of this modification can be expected to be rather low due to the inhomogeneity of the impregnation. This paraffin coating is reversibly adsorbed and can be removed with organic solvents [11].

It was shown that different surfaces can be hydrophobized in a simple desiccator using methyltrimethoxysilane (MTMS) by chemical vapor deposition (CVD) [13]. This approach avoids the use of solvents and elaborate wet chemistry and could allow for a very simple preparation of hydrophobized plates from normal-phase silica when needed. We hypothesized that a hydrophobization of polar, normal-phase silica plates with methyltrimethoxysilane by CVD should result in a uniform, hydrophobic stationary phase useful for thin-layer chromatography. These plates could be a readily prepared as inexpensive substitute for costly conventional reversed-phase plates. To be a suitable alternative, the plates would need to offer a separation performance that is competitive with both the commercial plates and the quickly prepared paraffin-coated plates.

2 Experimental

2.1 Consumables (silica plates and chemicals)

Silica gel thin-layer chromatography plates for normal-phase applications (TLC silica gel 60 F₂₅₄, NP-TLC) and C18 bonded silica plates (TLC silica gel 60 RP-18 F₂₅₄S, RP-18) were obtained from Merck (Darmstadt, Germany). Methyltrimethoxysilane (MTMS, 98%), ammonium hydroxide (28% in water), methyl 4-hydroxybenzoate (MP, > 99%), isobutyl 4-hydroxybenzoate (IBP, > 97%), and acetone (> 99%) were purchased from Sigma Aldrich (Schnelldorf, Germany). Ethyl 4-hydroxybenzoate (EP, > 99%), propyl 4-hydroxybenzoate (PP, > 99%), and butyl 4-hydroxybenzoate (BP, 99%), were bought from Alfa Aesar (Kandel, Germany). Water was deionized. All chemicals were used without further purification.

2.2 Preparation of reversed-phase silica TLC plates by chemical vapor deposition (RP-CVD)

Chemical vapor deposition (CVD) was adapted from earlier work [13]. Briefly, 10 cm × 10 cm NP-TLC silica plates were placed vertically against the inside wall of a desiccator with an internal volume of 10.5 L. Two single-use plastic Petri dishes containing 10 mL of either MTMS or NH₄OH were

placed in the center of the desiccator. The desiccator was closed, and the plates were exposed to the chemical vapors at room temperature for 42 h. For contact angle experiments, 2.5 cm × 7.5 cm NP-TLC plates were treated for 2, 3, 6, 17, and 48 h, respectively. After the treatment, the chemically hydrophobized plates (RP-CVD) were generously washed with deionized water to remove side products.

2.3 Preparation of paraffin coated reversed-phase silica TLC plates (RP-Paraffin)

Paraffin-coated plates were prepared as described elsewhere [8, 12]. In short, 10 cm × 10 cm NP-TLC silica plates were developed with a solution of paraffin oil (Nujol) in dichloromethane (7%, V/V) in a closed developing chamber. After development, the plate (RP-Paraffin) was dried at ambient conditions in a fume hood. It is worth noticing that a yellowish tint remained on the treated part of the plate.

2.4 Characterization

Fourier-transform infrared spectroscopy (FTIR) was performed with a PerkinElmer Frontier IR Single-Range spectrometer (Waltham, MA, USA) in ATR mode on the silica powder obtained by scratching the surface of the plates. All spectra were derived from 16 accumulated scans, each covering the wavelength range of 600–4000 cm⁻¹ at a resolution of 4 cm⁻¹. All spectra were baseline corrected and normalized to the highest peak.

Contact angle measurements (24 ± 2 °C, deionized water) were performed using a Drop Shape Analyzer (Krüss GmbH, Hamburg, Germany). Immediately after deposition of a water droplet (≈ 2 μL), pictures were acquired with a high-speed camera at a speed of 10 frames per second during two seconds to follow any changes in shape of the water droplet. The contact angles obtained for each frame were measured and averaged using the ellipse method of the Krüss Advance software package. For the sake of reproducibility, ten measurements were conducted at different locations on three plates per treatment.

Isothermal water sorption and desorption was studied with a Dynamic Vapor Sorption apparatus (DVS, Surface Measurement Systems Ltd, London, UK). 15–30 mg of powder scratched from TLC plates were placed in the chamber and were dried for 1 h at 0% relative humidity (RH) and 20 °C. Each experiment consisted of a sorption phase followed by a desorption phase. The sorption part was started by increasing the relative humidity stepwise (0%, 20%, 40%, 60%, 80% and 100% RH). Each step was started only after equilibration to a constant weight [14]. The desorption was performed in a similar way from 100% to 0% RH. During both directions of the experiment, the desired relative

humidity was obtained by mixing water vapor with nitrogen gas under a constant flow.

2.5 Chromatography

For RP-Paraffin and RP-18 plates, elution constants were determined with an HPTLC Vario system (CAMAG, Muttenz, Switzerland). For RP-CVD, the Vario system could not be used since no flow was achieved. Conventional vertical elution in typical TLC chambers was used instead for these plates. Further developments were conducted with an Automatic Developing Chamber (ADC 2, CAMAG).

Test solutions were prepared by dissolving 2.0 mg of each paraben (MP, EP, PP, BP, and IPB) in 10 mL of acetone. Samples (1 μ L) were sprayed as 8 mm bands at 100 nL/s with an Automatic TLC Sampler (ATS 4) equipped with a 25 μ L syringe. On the last position, one microliter of each paraben solution was sprayed to assess the separation. During spraying, the nozzle was heated to 60 °C. The application started at 10.0 mm from the bottom (*Y* axis) and 20.0 mm from the left side (*X* axis). Track distance was 11.4 mm. After each deposition, the syringe was rinsed with neat acetone. Humidity control and elution were performed in the ADC 2. Before elution, the plates were equilibrated for 20 min at 33% RH with a MgCl₂ solution. Elution was performed at 23 °C (± 1 °C) with acetone–water (*V/V*) mixtures with the following proportions: 60:40 for RP-18, 55:45 for RP-Paraffin and 65:35 for RP-CVD to a distance of 70 mm. Images were taken with a TLC Visualizer (CAMAG) under ultraviolet (UV) light at 254 nm (remission mode), auto exposure, gain 1. Scans of the plates were performed at 254 nm along the *Y* axis with a TLC Scanner 3 (CAMAG) with the following settings: scanning speed 20 mm/s, slit dimension 5 mm \times 0.2 mm, resolution of 100 μ m/step. All instruments were controlled with visionCATS 2.5 software (CAMAG). Three repetitions were performed for each plate type.

2.6 Calculations

After elution of the solvent front to a distance *l*, the migration distance of each analyte, *z*, and the width of the analyte spot, *w*, were extracted from the chromatograms.

Jurin's law gives an approximation of the capillary action:

$$h = \frac{2\gamma \cos\vartheta}{\rho g r_0} \quad (1)$$

with *h* being the liquid height, γ the surface tension of the solvent, ϑ the contact angle of the solvent on the material, ρ the mass density of the solvent, *g* the gravitational acceleration, and *r*₀ the diameter of the capillary.

The elution constant κ was calculated according to Eq. 2 [15] with the migration distance *z* fixed at 2.5 cm and measuring *t*, the migration duration in minutes:

$$\kappa = \frac{z^2}{t} \quad (2)$$

The theoretical number of plates, *N*, was obtained by Eq. 3 [11]:

$$N = \frac{16lz}{w^2} \quad (3)$$

with *z* being the migration distance (in mm), *l* the developing distance (in mm), and *w* the spot width (in mm).

Consecutively, the plate height, *H* (in μ m), was calculated by Eq. 4 [11]:

$$H = \frac{l}{N} \quad (4)$$

The resolution between two adjacent peaks 1 and 2 (with respective migration distances *z*₁ and *z*₂ and the widths of the spots *w*₁ and *w*₂), *R*_s, was defined by [11]:

$$R_s = \frac{z_2 - z_1}{0.5(w_1 + w_2)} \quad (5)$$

3 Results and discussion

3.1 Physical characterization

Infrared spectra provided an overview of the chemical composition of the investigated silica and of the changes effected by the CVD treatment (Fig. 1A). The prominent peak at 1059 cm⁻¹ is indicative of Si–O bonds. Interestingly, an overlapping peak was observed at 1025 cm⁻¹ for RP-CVD plates that could be explained by the increase of the proportion of Si–O–Si bonds at the surface of silica particles [16]. Furthermore, the peaks present at 1273 cm⁻¹ and 777 cm⁻¹ in the spectra of RP-CVD are evidence of the Si–CH₃ bonds. The latter peak is typically observed upon sol–gel synthesis of MTMS [17]. Additionally, the analysis of the region between 2700 and 3800 cm⁻¹ highlighted the proportion of adsorbed water (3000–3700 cm⁻¹) and C–H bonds (2900 cm⁻¹) (Fig. 1B).

For paraffin-coated silica plates (RP-Paraffin), the strong C–H stretching bands at 2925 cm⁻¹ and 2855 cm⁻¹ correspond to the CH₂ and CH₃ groups of the long aliphatic chains in paraffin oil. A broad O–H band is still present, confirming that the paraffin oil is only coating the silica particles without chemically converting the OH groups. For RP-18, sharper peaks are obtained for C–H stretching bands which correspond to the defined aliphatic chains that

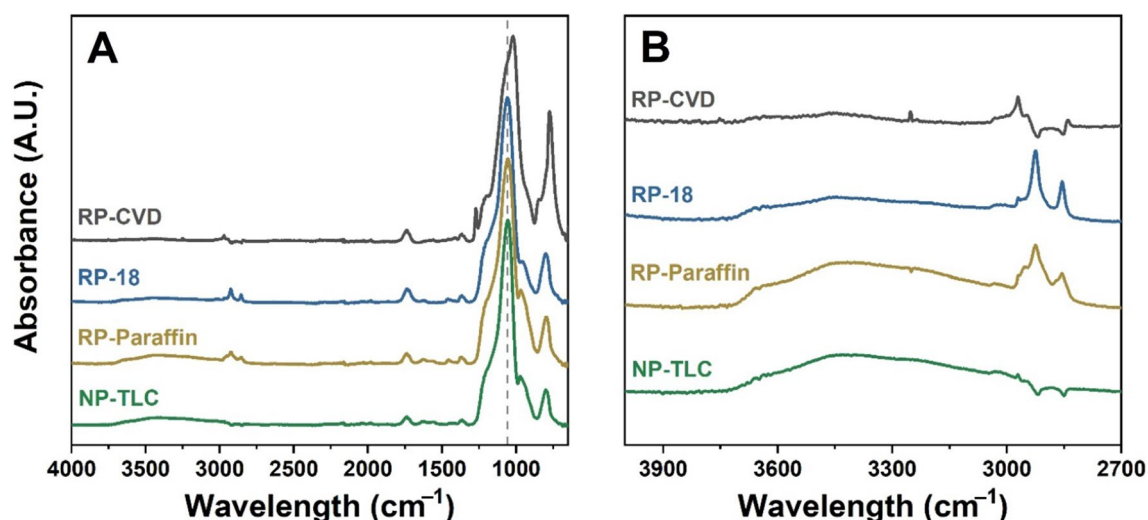


Fig. 1 ATR-FTIR spectra of NP-TLC, RP-Paraffin, RP-18 and RP-CVD silica gel plates (**A** from 600 cm^{-1} to 4000 and **B** zoomed range 2700 – 4000 cm^{-1})

derivatized the silica. As a consequence of the grafting of C_{18} chains onto silica that covered approximately 35% of silanol groups [18], the proportion of free hydroxyl groups decreased, which was visible by a flattened O–H peak. Finally, for RP-CVD, a small but sharp peak at 2970 cm^{-1} is characteristic of the introduced CH_3 moieties. The band of hydroxyl groups was practically undetectable, which mirrored the high hydrophobicity of the material.

In all measured spectra, a weak peak at 1735 cm^{-1} was present that did not correspond to any chemical bond found in siloxanes or alkanes. We assume that this peak can be assigned to the binder that is used in commercially available silica gel plates. This binder, typically poly(methyl methacrylate) (PMMA), contains ester moieties of which the $\text{C}=\text{O}$ stretching vibration would agree with the observed band.

Sorption isotherms provide information about the capability of the material to retain and release water. This is useful to assess the accessibility and number of hydroxyl groups in materials sensitive towards moisture [19–22]. The dynamic vapor sorption (DVS) isotherms of hydrophobized silica (RP-Paraffin, RP-18 and RP-CVD) and untreated silica are shown in Fig. 2. Obviously, the more hydrophobic plates—RP-CVD and RP-18—adsorbed very little water even at 100% RH, namely 3.3 wt% and 8.1 wt%, respectively. This indicated a low number of accessible hydroxyl groups. In contrast, RP-Paraffin exhibited a surprisingly large increase from 7 wt% to 50 wt% when relative humidity increased from 60% RH to 100% RH. Thus, a considerable number of hydroxyl groups remained accessible after the simple physical impregnation with paraffin. The highest amount of water was adsorbed by the untreated silica particles from NP-TLC, which retained more than 60 wt% water even at a relative humidity of 80%. Also, the hysteresis was more pronounced for the untreated

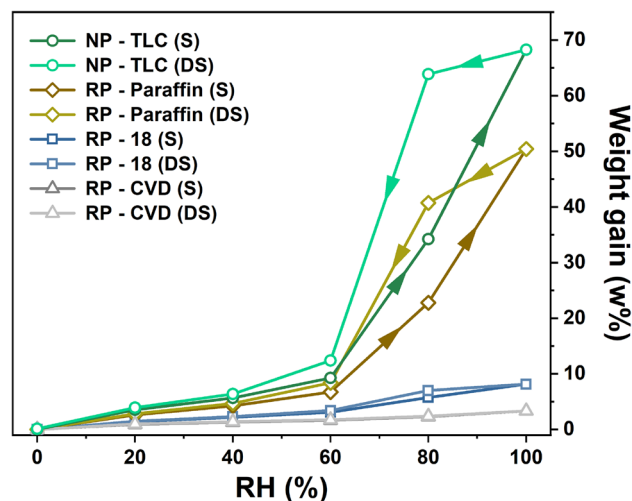


Fig. 2 Dynamic water vapor sorption (S) and desorption (DS) of aliquots scratched from NP-TLC, RP-Paraffin, RP-18, and RP-CVD silica gel plates starting from dried state (0% RH). All points were measured after equilibration between atmosphere and the aliquot to a constant weight

plates. Considering the ready adsorption of water to normal phase silica, it is evident that humidity can have a considerable effect on a planar separation system. It should be validated and adjusted as a parameter during optimization and needs to be controlled for reproducible results.

Determination of the water contact angle provides a direct measure of the hydrophobicity of a surface towards liquid water. Interestingly, a very short CVD treatment time, about 1 h, already resulted in a very hydrophobic material that showed strong water repellence (Fig. 3). In contrast, water did not even form a droplet on RP-Paraffin, RP-18, and

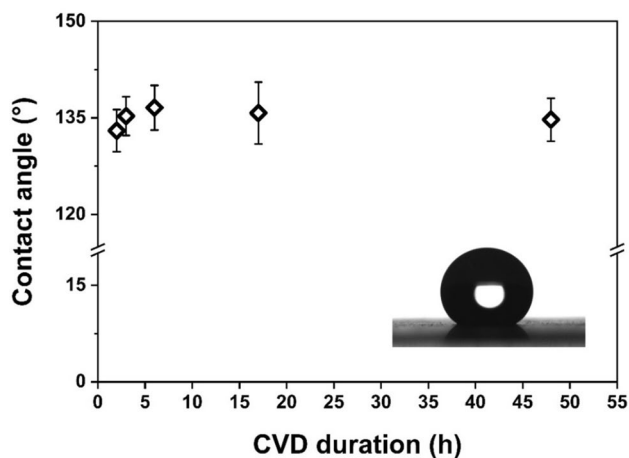


Fig. 3 Water contact angles versus duration of the CVD treatment

NP-TLC but was absorbed instantaneously; it was therefore not possible to measure a contact angle on these surfaces. While this is in agreement with the intuitive understanding of the “hydrophilic” NP-TLC and incompletely covered RP-Paraffin material, such a clear affinity to liquid water was not obvious for “hydrophobic” RP-18 plates. This demonstrates the decisive effect of a comparatively small number of residual hydroxyl groups.

Capillary action is the driving force of thin-layer chromatography. Its magnitude is described by Jurin’s law (Eq. 1), which relates the interaction between the liquid and a tube wall to the cosine of the contact angle. For the plates that could not sustain a water droplet, the contact angle is equivalent to zero, and the resulting cosine is 1. For contact angles above 90° , a negative cosine is obtained: thus, capillary flow will not happen spontaneously. Pure water can therefore not be used as eluent of the hydrophobized RP-CVD plates. By analogy to the other plates in the sample set, compatibility with pure water was achieved by reducing the extent of the treatment to retain non-reacted hydroxyl groups. The current, simple treatment setup had the disadvantage that it is not capable of precisely dosing the amount of reagent. It also gives little control over equilibration times during the initial saturation of the treatment chamber. The use of pure water was therefore not further investigated; instead, compatible eluents were prepared by mixing water with appropriate organic solvents.

The migration time for a given distance was recorded on RP-CVD-plates with several pure solvents to determine their elution constants, κ (Eq. 2; Fig. 4). In general, the constants followed the same order and were typically about 1/3 of the elution constants on regular normal-phase silica [15]. In addition, it was tested if mixtures of water with a miscible solvent can achieve capillary flow. Indeed, mixtures of water and methanol showed a flow on the RP-CVD plates, and the determined κ -values increased linearly with the percentage

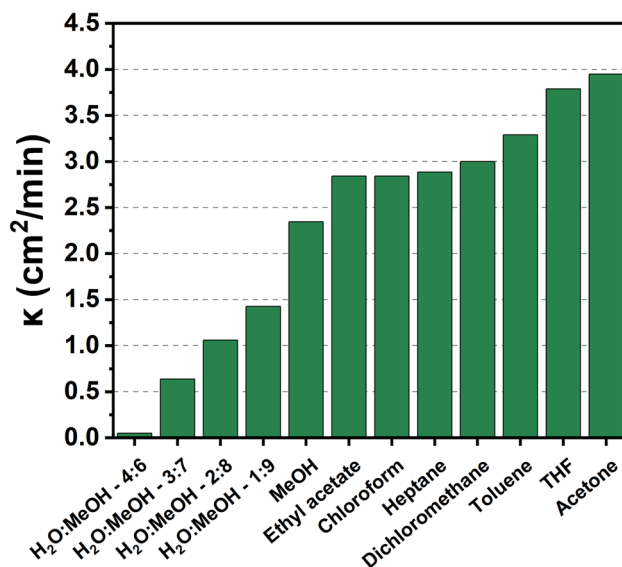


Fig. 4 Elution constants κ on RP-CVD plates of several solvents (MeOH–methanol, THF–tetrahydrofuran) and various mixtures of water and methanol. The elution duration was measured for a fixed elution distance of 2.5 cm (except H₂O–MeOH [4:6, V/V], which was stopped at 1.4 cm after 40 min of elution)

of methanol. By extrapolation, at least 59.5% methanol is required to achieve flow; this agrees with the minimal elution constant of $0.049 \text{ cm}^2/\text{min}$ observed for 60% methanol.

3.2 Chromatography

As established with methanol, water can be used as eluent on RP-CVD plates as a component of a binary solvent system. We selected acetone as eluent in the test systems with parabens, as it had the highest elution constant of the tested solvents and is miscible with water in any ratio. Wettability remained a major issue since it did not allow the use of eluent acetone–water mixtures with proportions of water above 45% (V/V).

Parabens (esters of *para*-hydroxybenzoic acid) are convenient test analytes, since they can be detected directly by fluorescence quenching or UV densitometry, and they are available as esters of various alcohols. We used a set with increasing lipophilicity, *i.e.*, methyl-, ethyl-, propyl-, isobutyl-, and butylparaben, that comprised two butyl isomers to test for regioselectivity in the separation. The separation of parabens on RP-18 plates is well described, as mentioned in the introduction. We used this test set to compare the performances of RP-Paraffin, RP-18 and RP-CVD plates.

The best separations of parabens in terms of resolution were obtained for solvent mixtures containing 35–55% acetone, depending on the plate. It was not possible to place all the peaks in the R_F range that theoretically gives the highest resolution (0.2–0.5, [9]), or to achieve more comparable

separations on these different stationary phases. All plates were developed to a solvent–front distance of 70 mm. Separations took a long time on all plates (see inserts in Fig. 5). For RP-CVD, this was expected; for the other two types of plates, a contributing factor might lie in the viscosity of the eluent mixture, which passes through its maximum in this compositional range. Also, acetone–water mixtures might provoke a strong swelling of the PMMA-based binder [11]. A possible yet untested remedy to reduce these elution times could be the addition of 3% NaCl (w/V) in the mobile phase [11].

Plate height (Fig. 6; Eqs. 3 and 4) and resolution (Fig. 7; Eq. 5) are two parameters that define the efficiency of the separation. They allow a direct comparison between the RP plates (see Table 1 in the Supplementary Information for the determined values). Small plate heights mean more efficient chromatographic systems, sharper peaks and stationary phases with the potential for a good separation. Resolution, in addition, takes the distance between peaks into account. Here, higher values indicate a better separation of the compounds.

The plate heights found for RP-CVD plates were quite consistent for all analytes, with averages from 60 to 80 μm , which are in agreement with the values reported for unmodified TLC plates [9]. Practically, these consistent plate numbers mean that the equilibration between stationary and mobile phase is of similar speed for all five analytes. The prepared stationary phase is suitable for chromatography and has the potential to yield narrower peaks than the other modified stationary phases. Also, the paraffin-coated plates showed consistent plate heights, albeit somewhat higher than the RP-CVD plates, with averages from 70 to 85 μm . RP-CVD plates should therefore give typically narrower peaks than paraffin coated ones. RP-18 plates gave very good plate heights for all parabens with propyl and butyl substituents—as low as those found for the RP-CVD plates—but showed distinctively higher plates (broader peaks) with higher variability for ethyl and methyl paraben. That the plate heights of RP-18 and RP-CVD plates are similar indicates that the structure and sizes of the particles and pores of the stationary phase were not deteriorated by the CVD treatment.

Surprisingly, the best values for resolution were observed for paraffin coated plates with values around 1. RP-18 achieved values around 0.75, and RP-CVD gave the lowest values at about 0.55. All systems struggled to separate *iso*-butyl and *n*-butyl paraben. For RP-Paraffin and RP-CVD, a slight separation is visible for the single standards but not in the mixture. For this regioselective separation to occur, the stationary phase must comprise rigidly positioned points of retentive interaction. This was apparently not the case for the RP-18 material while the other two modified plates still allowed some spatially characteristic interaction—most likely residual OH for RP-Paraffin and methyl for RP-CVD.

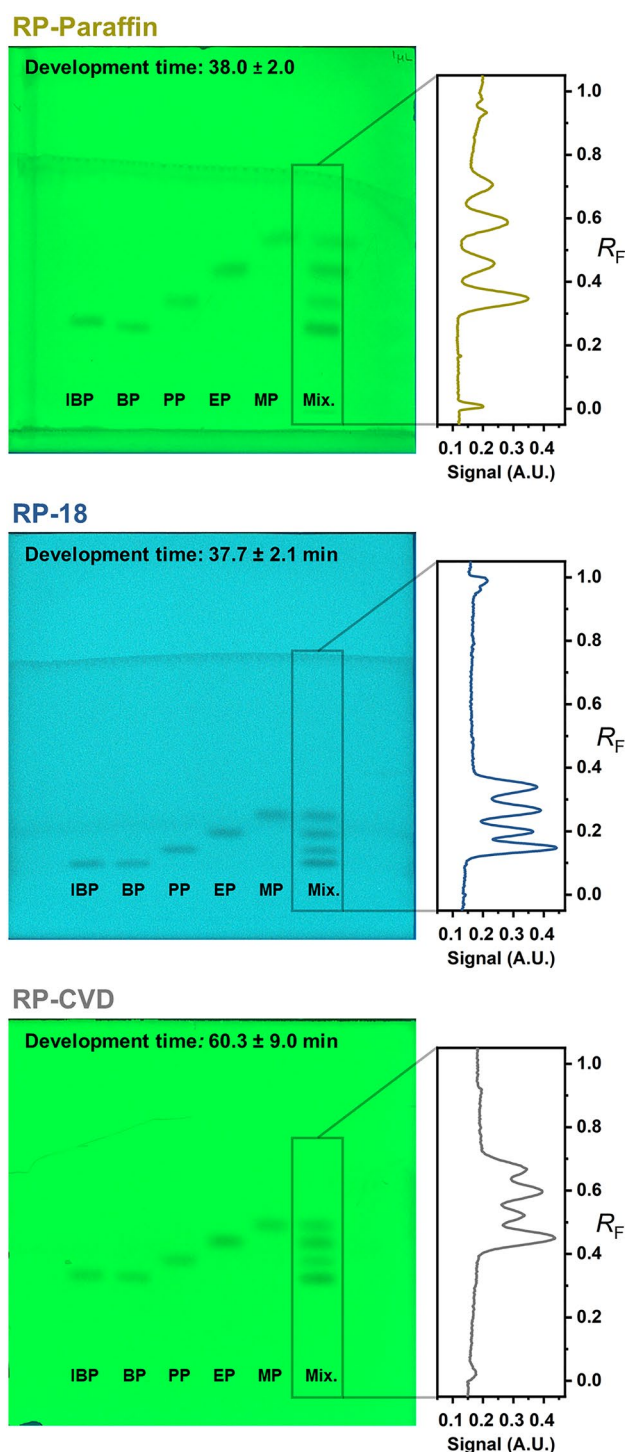


Fig. 5 Left part: chromatograms on RP-Paraffin, RP-18 and RP-CVD plates visualized by fluorescence quenching at 254 nm. The development times were determined in triplicate. From left to right, single parabens and their mixture were applied. Right parts: densitograms of the paraben mixture acquired at 254 nm

RP-CVD plates thus showed the potential to be a useful stationary phase for planar chromatography with a separation efficiency (plate height) equivalent to commercially

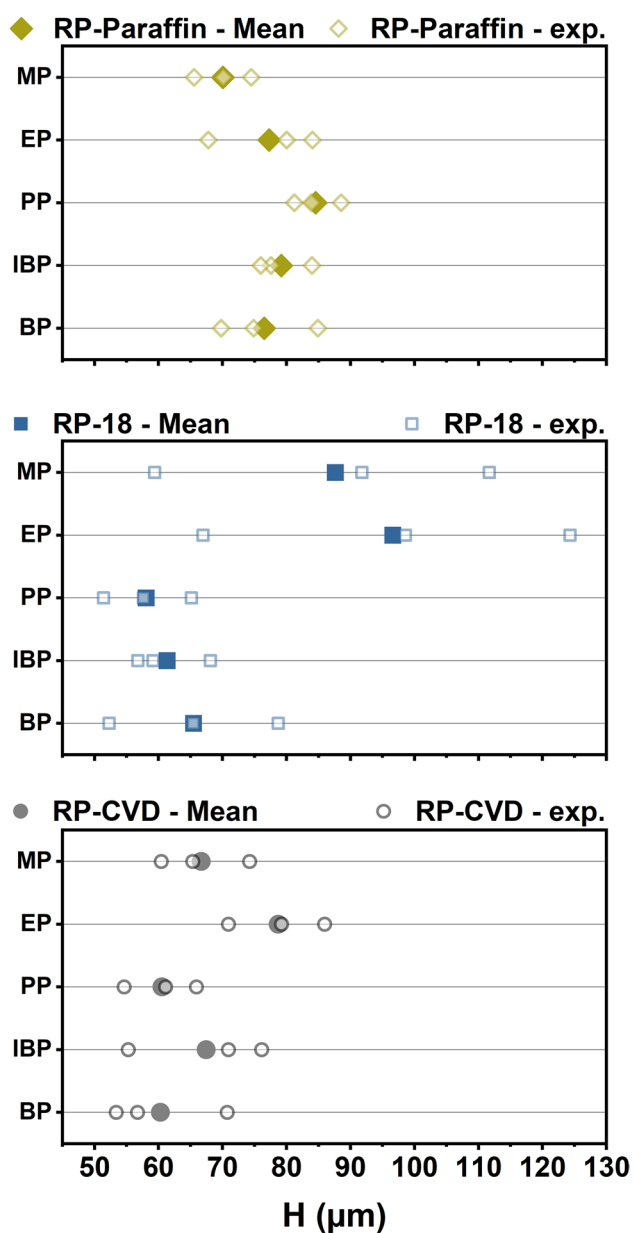


Fig. 6 Experimental (hollow dots) and mean (filled dots) values of plate heights (H) of methyl- (MP), ethyl- (EP), propyl- (PP), isobutyl- (IBP), and butylparaben (BP), comparing the performances of RP-Paraffin, RP-18, and RP-CVD plates

prepared hydrophobic plates. The highest obstacle to make full use of the plates' potential is in the choice of solvent to achieve reasonably short separation times.

4 Conclusion

Conventional plates for normal-phase thin-layer chromatography can be hydrophobized by chemical vapor sorption of methyltrimethoxysilane. The modification is resource

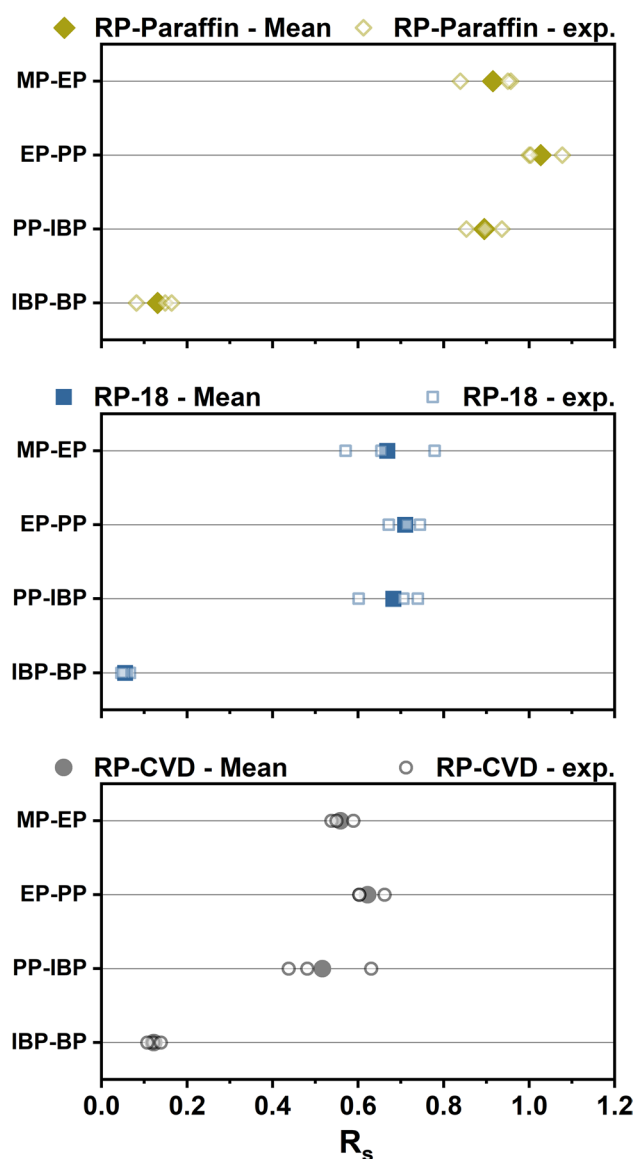


Fig. 7 Experimental (hollow dots) and mean (filled dots) values of resolution (R_s) of adjacent peaks between methyl- and ethylparaben (MP-EP), ethyl- and propylparaben (EP-PP), propyl- and *iso*-butylparaben (PP-IBP), and *iso*-butyl- and *n*-butylparaben (IBP-BP), comparing the performances of RP-Paraffin, RP-18, and RP-CVD plates

efficient, as no solvent or auxiliary besides some ammonia is required, and can be performed simply in a closed vessel. An exhaustive reaction of the reagent vapors with the accessible hydroxyl groups was observed by dynamic vapor sorption with water and by infrared spectroscopy: at 100% relative humidity, the treated plates adsorbed only 3 wt% water, and in the infrared spectrum, the characteristic hydroxyl group bands were almost invisible. The introduced substituent is covalently bound to the silica and cannot be washed away by organic solvents. A high water contact angle (close to 135°) was determined, thus the plates cannot be used with

pure water as eluent. Mixtures of water and organic solvents can be used. Keeping a certain level of non-reacted hydroxyl groups to increase wettability was not possible with the chosen setup. The elevated hydrophobicity of the plates leads to a generally low capillary action. Consequently, elution was slow, and analysis times were long.

The CVD-modified plates were tested with a homologous series of parabens, and the results were compared with a commercial C18 plate and a paraffin-coated plate. On all plates, the parabens were well separated with acetone–water as eluent. The determined heights of a theoretical plate were similar for all plates and in the range of the literature values. Paraffin-coating increased the plate height slightly, while the vapor-treated plates performed as well as the commercially modified ones. This indicates that the treatment does not have any detrimental effect on the material of the stationary phase. Both the paraffin-coated and the vapor-treated plates showed a slight separation of the isomers *n*-butylparaben and *iso*-butylparaben. This regioselectivity was not observed for C18 plates. It can be assumed that the plates feature slightly different separation mechanism, with the paraffin plate and the vapor-treated plate retaining some possibility for an adsorption mechanism that is not available on the C18 plate.

The study shows that a fast, technologically simple and cost-efficient vapor-phase treatment can result in an extensive surface modification of silica particles. That the substituents are covalently bound and fully cover the silica's hydroxyl groups could allow washing the plate quantitatively to be reused. The derivatization approach could be extended to other substituents with other alkoxy alkylsilane reagents to readily prepare a variety of stationary phases.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00764-023-00258-9>.

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Declarations

Conflict of interest The corresponding author, Stefan Böhmendorfer, is a member of the Editorial Board of the journal. Therefore, the submission was handled by a different member of the editorial board, and he did not take part in the review process in any capacity.

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