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Characterization of several stationary phases prepared by thermal immobilization of poly(methyltetradecylsiloxane) onto silica surfaces

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ABSTRACT

Variations of a thermal immobilization procedure using poly(methyltetradecilsiloxane) and silica produced fourteen stationary phases with carbon contents of 4–18%. The stationary phases were chromatographically evaluated with the Engelhardt, SRM 870 and Tanaka tests. Classifications using USP and Euerby procedures indicate that the new immobilized phases are different from most commercial phases although there was some similarity with phases that have high ion-exchange interactions. The retention mechanism involved in the separation of basic solutes on several of the new stationary phases was studied by varying pH, type of Lewis base and the ionic strength of the eluent. The separations are strongly influenced by the chemistry of the accessible free silanols. The stationary phases present good selectivity at intermediate pH where the basic analytes were protonated, suggesting use of intermediate pH for these separations. Stability tests show that the stationary phases have poor stability at very high pH, even at 23 °C, but good stability in acidic mobile phases, even at 75 °C, as expected for an immobilized polymer stationary phase.

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1. Introduction

Reversed-phase high performance liquid chromatography (RP-HPLC) is a well-known technique for the determination of many different types of compounds having different polarities, molar masses and functionalities, such as pharmaceuticals, pesticides and petrochemicals. RP-HPLC presents several advantages [1], including the use of less noxious and less expensive mobile phases, such as solutions of methanol or ethanol with water [2,3], fast equilibration of the column after changing the mobile phase, usefulness with gradient elution, high speed analyses and good repetitivity of retention times [4]. Stationary phases are the most important component of an HPLC system and, despite the large number of phases now available, the development of new stationary phases still occupies a prominent place in the literature [5]. Most commercially available stationary phases are prepared by chemical bonding C18 or C8 groups with the silanols of bare silica. However, novel phases can provide alternative and complementary separations for many analyses that are difficult to perform with C8 or C18 stationary phases. In many instances, the elution order of solutes differs on the novel phases, thus providing enhanced selectivity for difficult-to-separate compounds. This complementary approach can aid in identification, proof of purity, and quantitation [6]. Novel phases also offer chromatographers the flexibility to use simpler mobile phases, thereby avoiding ion pair reagents, exotic buffer systems, extreme pH conditions, and complex mobile phase preparations [7].

For a number of reasons, chromatographers also want to improve chemical and thermal stabilities, and thus the longevity of their stationary phases, and to adequately and quickly develop new analysis protocols by exploring all the experimentally available parameters, especially with respect to pH and temperature [8]. However, the range of these experimentally available parameters is very narrow since with silica-based stationary phases the support dissolves in alkaline mobile phases and the use of inorganic buffers (carbonate and phosphate) and temperatures equal to or higher than 60 °C increases the rate of dissolution [8].

Some novel phases present high chemical and thermal stabilities making possible the use of extreme pH mobile phases and higher temperatures [9]. Ethylene-bridged hybrid stationary phases from Waters [10] and polymer-coated zirconia stationary phases from ZirChrom [11–14] must be considered when highly alkaline mobile phases are required to change the selectivity of basic solutes or for solute stability reasons, especially when elevated temperatures are necessary to reduce analysis time [9]. These novel stationary phases show very different retention mechanisms. The former shows only hydrophobic interactions, while the latter has a mixed-mode separation mechanism. Although mixed-mode retention mechanisms in RP-HPLC are usually considered

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to be undesirable [15], good basic solute selectivities have been shown when polymer-coated zirconia columns are optimized for mixed-mode separations involving both hydrophobic and ionic interactions. It is possible to adjust selectivity by changing the type of buffer, the pH and the ionic strength of the eluent as well as the type and amount of organic modifier.

Similar to the approach taken by ZirChrom, another alternative for the preparation of stationary phases for HPLC consists of immobilizing linear polymer molecules into the silica pore system. Polysiloxanes are ideal for this application as the apparent distance between the monomeric units is nearly optimal for multipoint adsorption of the siloxane $(–Si–O–)_n$ chain onto the silica surface [16,17]. Stationary phases prepared by the immobilization of polysiloxanes onto silica have been shown to separate multiresidues of pesticides and their metabolic/degradation products (weak acids and bases), benzodiazepines and basic pharmaceuticals [16]. Similar phases have also been used for concentration and clean-up procedures using solid phase extraction [17].

The present paper describes the preparation and chromatographic evaluation of stationary phases by thermal immobilization of poly(methyltetradecylsiloxane) (PMTDS) onto silica (PMTDS–SiO_2). PMTDS was chosen as Szabó et al. [18] have suggested that the fourteen carbon chain, with a length intermediate between C8 and C18, should perform separations similar to those obtained with both these phases. The PMTDS–SiO_2 stationary phases were evaluated initially with some classical tests such as the Engelhardt [19], SRM 870 [20] and Tanaka tests [21]. These results were compared with literature data [22–25] for commercial phases to obtain an idea of their chromatographic behavior. One of the stationary phases with intermediate carbon content was evaluated with a in-house test that evaluated the effect of different pH, buffer type and buffer concentration on retention factors and asymmetry factors of several basic solutes (hydrophobic and hydrophilic), as proposed Carr and co-workers [11–14]. The importance of the ion exchange mechanism to the retention was evaluated using mobile phases with different phosphate buffer concentrations. The chemical and thermal stabilities were also evaluated at both high [8] and low [26] pH. Finally, the applicability of the PMTDS–SiO_2 stationary phases was compared with that of a stationary phase with the same carbon content prepared by the thermal immobilization of poly(methyloctylsiloxane) onto the same silica using both isocratic and gradient mode elutions.

2. Experimental

2.1. Chemicals and reagents

The mobile phases were prepared with ultrapure water from a Millipore Direct-Q™ system (Billerica, USA). Methanol and isopropanol were from Tedia (Fairfield, USA). Tetrahydrofuran was from J.T. Baker (Phillipsburg, USA). Pentane was purchased from Merck (Darmstadt, Germany).

The reagents used to prepare the mobile phases were: KH_2PO_4 (98%), K_2HPO_4 (99%) and $KHCO_3$ (99.7–100.5%) from Synth (Diadema, Brazil), sodium citrate tribasic dihydrate (99%) and N-(2-hydroxy-1,1-bis(hydroxymethyl)ethyl)glycine (99%) (tricine) from Sigma (St. Louis, USA), sodium borate was from Fisher (Fairlawn, USA), triethylamine (99%) (TEA) and trifluoroacetic acid (99.5%) (TFA) from Vetec (Duque de Caxias, Brazil). 2-Amino-2-hydroxymethyl-propane-1,3-diol (Tris) from Mallinckrodt (Paris, France), ammonium hydroxide (28–30%) from LabSynth (Diadema, Brazil).

The silica was Kromasil, lot no AT 1959, from Akzo Nobel (Bohus, Sweden) with 5 μm particle size, 11.1 nm pore size and 313 m^2/g specific surface area. Kromasil is a type B silica that has only a small amount of contaminant metals. The polysiloxanes used were poly(methyltetradecylsiloxane), average molar mass (*M*) 9500, from Petrarch/Huls America (Piscataway, USA) and poly(methyloctylsiloxane), number-average molar mass, M_n, 6200, and weight-average molar mass, M_w, 16,000, from United Chemicals Technologies (Bristol, USA).

Table 1
Percentage of PMTDS per gram of silica (%PMTDS), time (*t*) and temperature (*T*) of immobilization used to prepare the stationary phases, %C from elemental analysis, and the final percentage of PMTDS per gram of silica after thermal immobilization (%$PMTDS_f$).

Code	%PMTDS	*t* (h)	*T* (°C)	%C	%$PMTDS_f$
SP1	30	4	100	4	6
SP2	60	4	100	5	7
SP3	30	8	100	6	9
SP4	60	8	100	15	21
SP5	30	4	130	9	13
SP6	60	4	130	10	14
SP7	30	8	130	18	26
SP8	60	8	130	19	27
SP9	20	6	115	8	11
SP10	70	6	115	9	13
SP15	45	6	115	8	11
SP16	45	6	115	9	13
SP17	45	6	115	11	16
SP18	45	6	115	10	14

The test solutes were: uracil (98%), butylbenzene (>99%) and amitriptyline hydrochloride (99%) from Aldrich (Milwakee, USA), benzylamine (>99%), pentylbenzene (>98%) and o-terphenyl (>99%) from Merck-Schuchardt (Hohenbrunn, Germany), caffeine from Medley (Campinas, Brazil), phenol (>99.5%), N,N-dimethylaniline (≥98%) and triphenylene (≥98.0%) from Fluka (Buchs, Switzerland), aniline (99.5%) from Merck, ethyl benzoate (99%) from Carlo Erba (Milan, Italy), HPLC grade toluene from Tedia (Rio de Janeiro, Brazil), and p-ethylaniline (98%), ethylbenzene (99%), quinizarin (96%), nortriptyline hydrochloride (98%), dextromethorphan hydrobromide, (−)-nicotine (98–100%) and (±)-chlorpheniramine maleate salt from Aldrich (Steinheim, Germany). Codeine sulfate, diphenhydramine hydrochloride, propanolol, salbutamol sulfate and methadone were kindly donated by Dr. Marcelo Ribani from TECPAR (Curitiba, Brazil) while the benzodiazepines and fluoxetine were kindly donated by Dr. Paulo César Pires Rosa of EMS (Hortolândia, Brazil).

2.2. Preparation of the stationary phases

The PMTDS–SiO_2 stationary phases were prepared using different amounts of PMTDS (g PMTDS/g silica), and different times (h) and temperatures (°C) of thermal treatment, as summarized in Table 1. The general procedure for the preparation of these stationary phases consists in dissolving PMTDS in 20 mL of pentane, then adding 1 g of Kromasil silica and 20 mL more of pentane. This mixture is stirred for 30 min at room temperature and then placed in a fume hood for the evaporation of the solvent at room temperature. The dried materials are then placed individually in an oven at the specified temperature for immobilization under an air atmosphere. The PMOS-SiO_2 stationary phase with carbon content of 18% was prepared as described elsewhere [27].

The stationary phases were slurry packed (0.8 g of stationary phase in 20 mL of 20:80 (v/v) isopropanol–tetrahydrofuran) into previously polished 50 mm × 4 mm columns [28] made from 316 stainless steel tubing at a constant packing pressure of 40 MPa, using a Haskel Packing Pump (Burbank, USA) with methanol as propulsion solvent. The pressure was maintained until the passage of 200 mL methanol to assure a good packing and removal of excess polysiloxane [29].

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