# Synthesis and Characterization of Diatomaceous Earth Chemically Modified with *n*- trichlorooctadecylsilane

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*A new stationary phase for thin-layer chromatography has been prepared by bonding purified diatomaceous earth from Minis-Romania (reach in silica) with n trichlorooctadecylsilane. The phase has been characterized by elemental analysis, specific surface area measurement, FTIR spectroscopy, thermal analysis and chromatographic testing.*

*Keywords: TLC, reversed-phase chromatography, diatomaceous earth, n-trichlorooctadecylsilane*

The presence of a high hydroxyl groups concentration with increased reactivity on the surface of Minis diatomaceous earth allows covalent linking with many groups that have different functions (organo-functional modifiers) thus obtaining new stationary phases for chromatography [1,2].

In order to obtain new chemically modified stationary phases, the adsorbent surface must meet the following conditions [3]:

-it must contain a maximum number of OH groups / surface unit (the adsorbent surface must be completely hydroxylated);

-the adsorbed water must be completely removed to avoid the formation of silicoorganic polymers physically adsorbed by hydrolysis or by modifier condensation;

-it must not contain impurities that modify stationary phase white degree (especially for thin layer chromatography).

Two types of problems occur and must be taken into consideration while obtaining chemically modified stationary phases, one being preparation reproducibility and the other one being phase stability.

The methods for chemical binding of the modifier onto the support material are based on four types of chemical links [1, 4, 5]:

-Si-O-C ester links;

-Si-C link;

-Si-N links;

-Si-O-Si-C siloxane links.

The Si-N, Si-C and Si-O-C links have a reduced stability compared to siloxane links (Si -O- Si -C). The last are the most frequently used for stationary phases production. The siloxane links are obtained by the organosilanization reaction that is consisting in the X functional group action (X = $-OC_2H_5$, $-OCH_3$, -OH, -Cl, -H, $-OCOCF_3$, $-N(CH_3)_3$ etc.) of a substituted organosilane ($R_1R_2R_3SiX$) onto the superficial silanol groups from the silica gel.

Depending on the water presence during the synthesis and on the reaction conditions, monomeric, polymeric or oligomeric stationary phases can be obtained, which have different characteristics [2,4]. Monomeric phases are obtained using mono-, di- or trifunctional silanes in the absence of water traces[6-8], and display the aspect of a chemically bonded monomolecular layer on the adsorbent surface where the chain distribution is not uniform [9-11].

The chemical modification reaction of the adsorbent surface, for the monomeric phases, consists in the chemical linking of one end of the liquid molecules from the stationary phase with the suport grain surface. Depending on the temperature and the solvent used, the structural groups (alkyl, phenyl etc.) of the modifier can have any conformation from a brush structure, with molecules linked perpendicularly on the suport by covalent links, to a liquid type structure where linked chains fill the closest space from the suport surface [9-11].

Due to steric reasons about 50% of the silanol groups are unable to react. The coverage degree varies depending on the suport surface OH groups number and on the reaction conditions. Therefore, for the metallic oxides (alumina, titania, zirconia) the coverage degree was 1.5-1.7 $\mu mol/m^2$ [12] and for the octadecylsilane between 3.09-6.45 $\mu mol/m^2$ [13].

The presence of water traces in case of a three organosilane functions leads to a polymerization on the adsorbent surface because the newly created silanol groups can react with the modifier [1,6,10]. The molecular structure of polymeric phases is not well defined and can be described as a cluttered poly molecular layer which covers the support surface [8]. The polymeric stationary phases have low efficiency because the diffusion coefficients of the solutions are lower than for monomeric phases, and also have reproducibility problems because of the difficult control over the water content and over the polymerization degree [8]. The polymeric stationary phases have some advantages against monomer phases because they have increased stability to hydrolysis and partial shielding against some unwanted properties of the support surface, like the presence of silanol groups and residual acids.

Oligomeric phases can be obtained by careful control of the different phases of the silanization reaction. The

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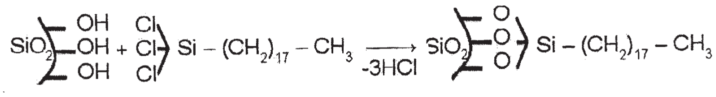


Fig. 1 Synthesis reaction of n-octadecyl modified diatomaceous earth

reaction of dichlorosilane with the silanol groups of the support can take place under anhydrous conditions, followed then by the hydrolysis reaction which leads to the obtaining of a monomeric phase. The obtained modified stationary phase is silanized again with the same dichlorosilane, thus resulting different polymeric layers [8]. The synthesis of oligomeric phases is, basically, a controlled sequential polymerization, each stage being a monomer synthesis [14, 15].

The interest for obtaining new n-octadecyl chemically modified stationary phases did not diminish over the last years, on the contrary it increased and this fact can be noticed from the published specialty studies [16-21]. The lab experiments aimed for the chemical modification of the Minis diatomite earth surface with n-octadecyl-trichlorosilane, the physico-chemical characterization of the obtained product, the chromato-graphic behaviour and the use of this product as a stationary phase in thin layer chromatography.

## Experimental part

### *Chemicals*

All reagents were obtained from commercial sources: HCl, xylene, methylene chloride, anhydrous ethyl ether, toluene, n octadecyltrichlorosilane, KBr, acetonitrile, $H_3PO_4$ 75% (Merck), benzodiazepines (Fluka), Barium and Magnesium Aluminate activated with Europium, Ytrium Aluminate activated with Cerium (Institute of Chemistry Cluj-Napoca, Romania).

### *Synthesis of n-octadecyl chemically modified Minis diatomaceous earth stationary phase*

The *n*-octadecyl chemically modified Minis diatomaceous earth was obtained from the reaction of micronized Minis diatomaceous earth that was purified with hydrochloric acid with the n-octadecyltrichlorosilane modifier. The idealized synthesis reaction is shown in figure 1.

The *n*-octadecyl chemically modified diatomaceous earth was obtained in a similar installation. 100 g of purified and activated Minis diatomaceous earth were inserted in the flask together with 400 mL xylene (o, m, p) as reaction medium. After the temperature of the mixture in the reaction flask reached 60°C, 42 mL of n octadecyl-trichlorosilane were added by drops trough the feeder ($\rho_{20^{0}C}$=0.98 g/cm$^3$). The reaction lasted 4 hours at 60°C in nitrogen atmosphere, the mixture being continously stirred. The resulted product was cooled, vacuum filtered (with the help of a vacuum pump) and succesively washed with xylene, methylene chloride, anhydrous ethyl ether and dried under vacuum. The obtained stationary phase is a white powder immiscible with water.

### *Physico-chemical and structural characterization*

Coverage density of the chemically modified diatomaceous earth was obtained by using following formula [7, 22]:

$$\alpha = 10^6 \cdot C/(1200N-CM).S \ (\mu mol/m^2)$$

where:

C-% carbon measured by elemental analysis;

N- no of carbon atoms from ligand;

M-relative molecular mass of the ligand unit;

S- specific surface of unmodified diatomaceous earth. The specific surface area was measured by adsorption of krypton at liquid nitrogen temperature.

FTIR spectra were recorded with a resolution of 4 cm$^{-1}$ in the 4000-400 cm$^{-1}$ spectral domain using the well-known KBr pellet technique.

The thermo analytical curves for unmodified and n-octadecyl modified diatomaceous earth were recorded with a TG-DTA-DTG Mettler Toledo device, in the 25 – 1100$^0$C temperature interval, with a 5$^0$C/min heating speed in nitrogen atmosphere with 5 L/h flow. Aluminium nacelles and approximately 30 mg of the sample were used for the measurements.

The *n*-octadecyl chemically modified Minis diatomaceous earth is a white powdered, with a white degree of 94.2%, which allows the separation and detection of compounds by thin layer chromatography. In order to test the n-octadecyl chemically modified Minis diatomaceous earth for thin layer chromatography usage, glass chromatographic plates of 10x10 cm dimensions were prepared with a 0.3 mm layer thickness. The paste deposited onto the glass plates contained 5% organic binder and was prepared by mixing 4 parts Barium and Magnesium Aluminate activated with Europium ($BaMg_2Al_{16}O_{27}$:Eu), 3 parts Ytrium Aluminate activated with Cerium ($Y_3Al_5O_{12}$:Ce) and 100 parts *n*-octadecyl modified diatomaceous earth with propylpyrolidone dissolved in ethylic alcohol [23].

Standard solutions (0.1%) of six benzodiazepines were prepared in ethylic alcohol. Volumes of μL/spot were applied onto $C_{18}$ Merck Silica gel chromatographic plates and *n*-octadecyl modified diatomaceous earth chromatographic plates. The plates were developed at a 7 cm distance by the ascending technique, with an acetonitrile-water- $H_3PO_4$ 75%, 50:50:1, v/v mobile phase.

Seven polyphenols (rosmarinic acid, o-coumaric acid, p-coumaric acid, caffeic acid, gallic acid, quercetin and rutin) were separated onto TLC silica gel 60 RP 18 $_{F254}$plates using acetic acid 1M-methanol (70:30 v/v) as mobile phase.

## Results and discussions

### *Characterization of n-octadecyl chemically modified diatomaceous earth*

FTIR spectroscopy, thermoanalytical studies, coverage density studies and chromatographic behaviour studies were made in order to conduct the physico-chemical characterization of the *n*-octadecyl chemically modified diatomaceous earth.

### *Coverage density*

Table 1 shows the results for „α" coverage density, elemental analysis (Carbon, Hydrogen) and specific surface area measurements (BET method).

**Table 1**

n-OCTADECYL CHEMICALLY MODIFIED MINIS DIATOMACEOUS EARTH PROPERTIES (%C; %H; –$S_{BET}$ SPECIFIC SURFACE; α COVERAGE DEGREE)

| Stationary phase | Carbon (%) | Hydrogen (%) | $S_{BET}$[$m^2g^{-1}$] | α (μmol/m$^2$) |
|---|---|---|---|---|
| Minis diatomaceous earth | - | - | 146.1 | - |
| Modified Minis diatomaceous earth | 9.63 | 2.63 | 50.20 | 3.69 |

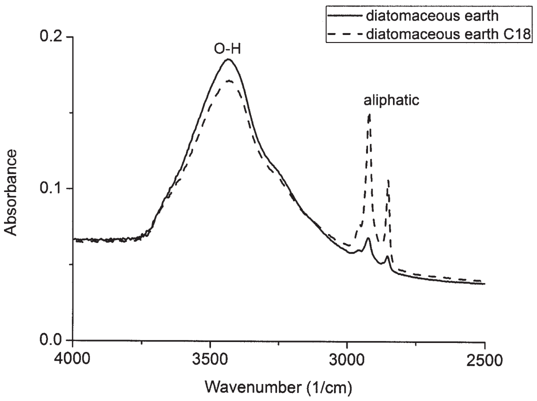


Fig. 2 FTIR spectra in the 4000-2500 cm$^{-1}$ spectral region for unmodified Minis diatomaceous earth (solid line) and n-octadecyl modified Minis diatomaceous earth (dash line)

Table 1 shows that the n-octadecyl chain is comprised in the *n*-octadecyl modified diatomaceous earth. By chemically modification of the diatomaceous earth the specific surface decreases from 146.1 to 50.2 m$^2$g$^{-1}$. Coverage density of 3.69 μmol/m$^2$ shows a good area coverage for the n-octadecyl chemically modified diatomaceous earth. The obtained results are in agreement with the literature[13, 17].

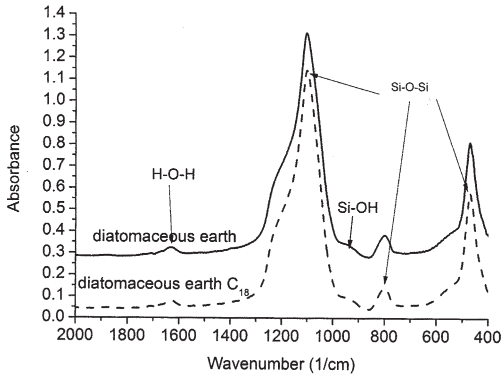


Fig. 3 FTIR spectra in the 2000-400 cm$^{-1}$ spectral region for unmodified Minis diatomaceous earth (solid line) and n-octadecyl modified Minis diatomite earth (dash line)

### *FTIR spectroscopy*

FTIR spectra of unmodified and *n*-octadecyl modified diatomaceous earth, recorded with KBr pellets technique, are shown in figures 2 and 3.

The FTIR spectrum of *n* octadecyl chemically modified diatomaceous earth (dash line) shows the superficial modifications after the organosilanization reaction of Minis diatomaceous earth with *n* octadecyltrichlorosilane:

-the presence of the modifier n-octadecyl chain is highlighted by the new 2800-3000 cm$^{-1}$ bands presence, characteristic for methylene vibrations (-CH$_2$-);

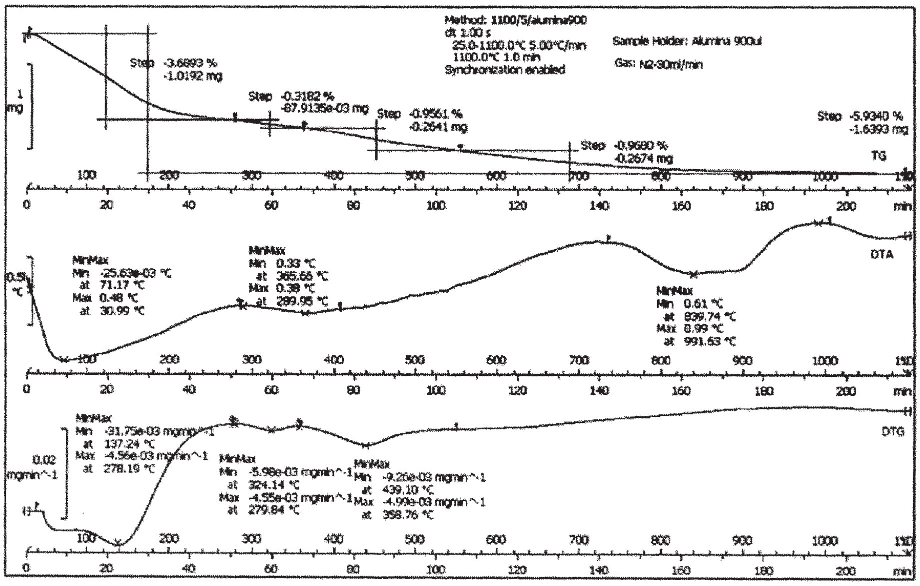


Fig. 4 Thermogravimetric curves for unmodified Minis diatomaceous earth

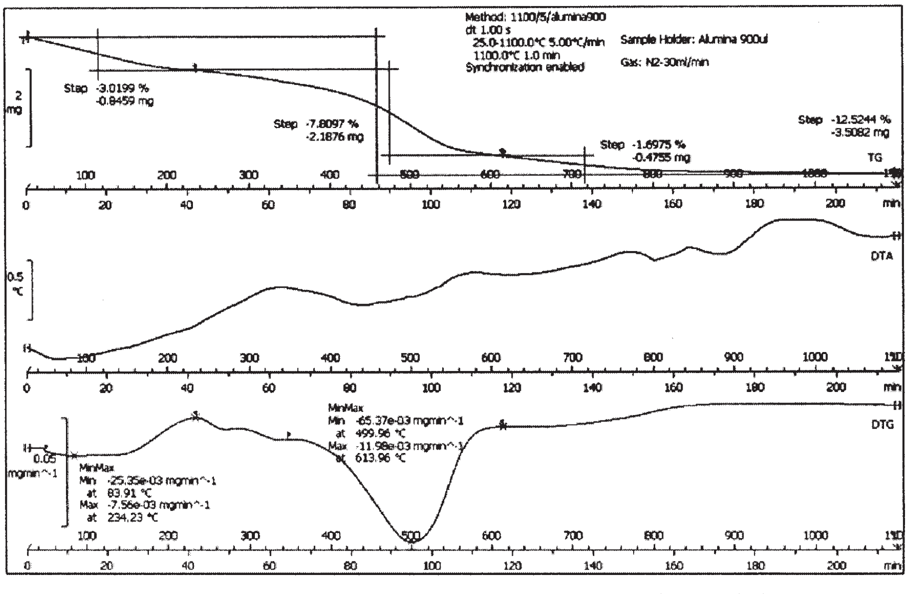


Fig. 5 Thermogravimetric curves for n-octadecyl modified Minis diatomaceous earth

-the silanol groups reduction after the silanization reaction is shown by the ν(OH) band intensity decrease in the 3200-3600 $cm^{-1}$ spectral domain.

*Thermoanalytical study*

The TG, DTA and DTG thermoanalytical curves for the unmodified diatomaceous earth are shown in figure 4 and in figure 5 for the *n*-octadecyl modified diatomaceous earth.

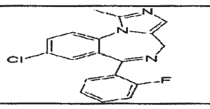
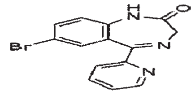
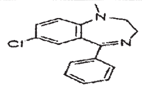
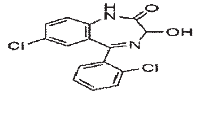
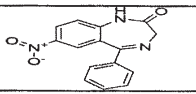
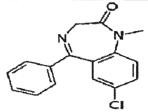
By analyzing the two figures, for the unmodified diatomaceous earth can be noticed a 3.69% loss in the 25-$280^0$C interval that represents the physically adsorbed water, and in the 280-$1100^0$C interval a 2.24 % loss that represents the chemically bonded water, the silanol groups condensation to siloxane with water elimination and a number of inorganic compounds which are volatilized at this temperature ($FeCl_3$, oxides etc.). In the case of the modified diatomaceous earth the losses in the 25-$240^0$C temperature interval are smaller as compared to those for unmodified diatomaceous earth, but in the 240-$619^0$C interval the modified diatomaceous earth the mass losses are very high (7.81%) showing the burning of the chemical modifier. This shows that the n-octadecylsilane modifier was linked to the Minis diatomaceous earth. This is also shown in the DTG diagrams. For the unmodified Minis diatomaceous earth there is a minimum at $137.24^0$C which represents the physically adsorbed water elimination, a minimum at $324.14^0$C which represents the chemically bonded water elimination and a minimum at $439.10^0$C which represents the silanol group condensation to siloxane, with water elimination. The DTG diagram for the n octadecyl modified diatomaceous earth contains only two minimums, one at $439.10^0$C where traces of solvents present in the adsorbent are eliminated, and one at $499.96^0$C where the chemical modifier is eliminated by burning.

*Chromatographic behaviour*

Table 2 data shows that separations made on n-octadecyl modified diatomaceous earth are similar with those made on $C_{18}$ Merck Silica gel.

**Table 2**

$R_F$X100 VALUES OF SOME BENZODIAZEPINES SEPARATED ON $C_{18}$ MERCK SILICA GEL AND n-OCTADECYL MODIFIED DIATOMACEOUS EARTH, USING ACETONITRILE-WATER-$H_3PO_4$ 75% (50:50:1, v/v) MIXTURE AS MOBILE PHASE

| **Nr. Crt.** | **Commercial name** | **Chemical name** | **Structural formula** | $R_F$ x $100^*$ | $R_F$ x $100^{**}$ |
|---|---|---|---|---|---|
| 1 | Midazolam | 8-chloro-6-(2-fluorophenyl)-1-methyl-4*H*-imidazo[1,5-a][1,4]benzodiazepine |  | 47 | 59 |
| 2 | Bromazepam | 9-bromo-6-pyridine-2-yl-2,5-diazabiciclo [5.4.0]undeca- 5,8,10,12-tetraen- 3-one |  | 41 | 56 |
| 3 | Medazepam | 9-chloro-2-methyl-6-phenyl-2,5-diazabiciclo[5.4.0]undeca-5,8,10,12-tetraene |  | 35 | 52 |
| 4 | Lorazepam | (*RS*)-9-chloro-6-(2-chlorophenyl)-4-hydroxi-2,5-diazabiciclo[5.4.0]undeca-5,8,10,12-tetraen-3-one |  | 28 | 45 |
| 5 | Nitrazepam | 9-nitro-6-phenyl-2,5-diazabiciclo[5.4.0]undeca-5,8,10,12-tetraen-3-one |  | 38 | 56 |
| 6 | Diazepam | 7-chloro-1,3-dihydro-1-methyl-5-phenyl-1,4-benzodiazepin-2(3*H*)-one |  | 31 | 40 |

* $C_{18}$ Merck Silica gel plates; ** n-octadecyl modified diatomaceous earth plates

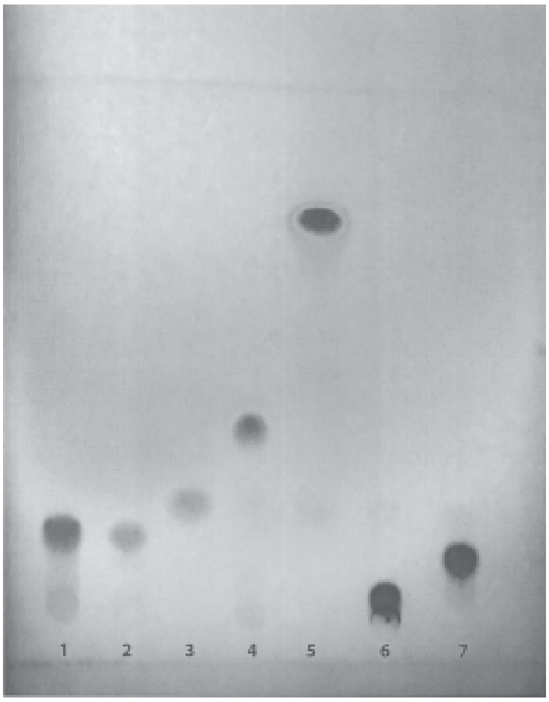


Fig 6 Chromatogram at λ = 254 nm for: 1 – rosmarinic acid; 2 – o-coumaric acid; 3 –p-coumaric; 4 – caffeic acid; 5 – gallic acid; 6 – quercetin; 7 – rutin. Stationary phase: silica gel 60 RP 18 $F_{254}$; mobile phase: acetic acid 1M–methanol, 70:30 v/v

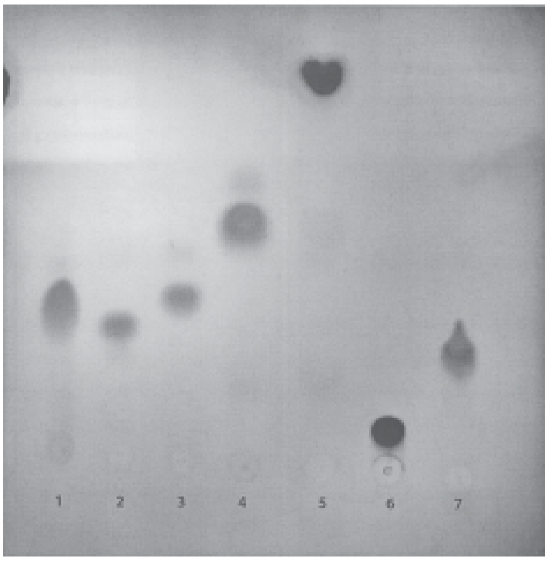


Fig. 7 Chromatogram at λ = 254 nm for: 1 – rosmarinic acid; 2 – o-coumaric acid; 3 –p-coumaric; 4 – caffeic acid; 5 – gallic acid; 6 – quercetin; 7 – rutin. Stationary phase: n-octadecyl modified Minis diatomaceous earth; mobile phase: acetic acid 1M–methanol, 70:30 v/v

The benzodiazepines separated on *n*-octadecyl modified diatomaceous earth have the same order as on $C_{18}$ Merck Silica gel but the $R_F$ values are greater and can be explained by the fact that the diatomaceous earth surface (146.1 $m^2g^{-1}$) is smaller than the Merck silica gel surface (500 $m^2g^{-1}$) and thus the coverage degree is smaller. The separation reproducibility is better for chemically modified diatomacous earth as compared to that for Silica gel $C_{18}$.

Figure 6 presents the seven separated polyphenols onto plates with C18, whereas figure 7 the same polyphenols are separated onto plates with diatomaceous earth chemically modified with *n* octadecyl.

Based on the analysis of these two chromatograms one can see similar separations obtained on these two type plates. The small differences in separations as concerned the diatomaceous earth modified plates are due to the lower specific surface of diatomaceous earth as compared to silicagel chromatographic supports.

## Conclusions

The data obtained from the studies are showing that, by modifying the surface of the diatomaceous earth with *n*-octadecyltrichlorosilane, its hydrophile character becomes hydrophobic, thus a new stationary phase being formed with physico-chemical characteristics and chromatographic behaviour that allows it to be used in thin layer chromatography as a reversed phase for separation and identification of organic and inorganic compounds. The separation reproducibility for chemically modified diatomacous earth is better than that for Silica gel $C_{18}$.

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