The separations using pure water as a mobile phase in liquid chromatography using polar-embedded stationary phases

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ABSTRACT
Following the idea of green chemistry, especially green analytical chemistry, a series of stationary phases was synthesized. The obtained materials connect polar and hydrophobic groups in the structure of bonded ligands. These specific surface properties provide the stability of the stationary phase in pure water as a mobile phase. To confirm the solvation ability in purely aqueous mobile phases, excess isotherms of water and acetonitrile were determined. Further, the mixtures of nucleosides, nucleic bases and purine alkaloids were applied to test the separation selectivity of stationary phases in purely aqueous conditions at ambient temperature without any additives to the mobile phase. Among the four tested stationary phases, it is possible to find one for separation of each group of analytes that offers selective separation in reasonable time. The presented data confirms that it is possible to synthesize stationary phases for the separation of target mixtures in pure water conditions.

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1. Introduction
Liquid chromatography (LC) is a common analytical technique. Analyses in liquid chromatography are performed in three modes: normal phase liquid chromatography (NP LC), reversed phase liquid chromatography (RP LC) and hydrophilic interactions liquid chromatography (HILIC) depending on the polarity of solutes to separate. However, liquid chromatographic analyses generate a significant amount of organic solvents waste, such as methanol, acetonitrile and nonpolar solvents.

Over the recent years, green analytical chemistry has been developed to reduce or remove the use of environmentally hazardous organic solvents and reagents (1–6). The well-known principles of green chemistry (1), three Rs (Reduce, Replace, Recycle) are commonly used in the field of analytical chemistry methods, including chromatographic analyses. The most important direction to make analytical chromatography more environmentally friendly is the replacement of hazardous solvents. It may be done using more green alternatives of solvents or by the reduction of the amount of generated organic waste (2, 7). As an example, ethanol may be used instead of acetonitrile in RP LC. Unfortunately, such greener solvent is usually less effective (8). The most interesting idea is to use pure water as a mobile phase (9, 10). This idea may be realized at a normal, elevated and subcritical temperature (11–20). An alternative to purely aqueous HPLC may be the supercritical fluid chromatography with pure water (21–23). However, the application of pure water in typical reversed-phase chromatography is usually associated with phase collapse, non-repeatable retention times, peak tailing. In this case using an apolar...
stationary phase such as C18 does not ensure enough retention towards polar compounds (24, 25).

The clarified methods, that have been applied in liquid chromatography in recent years to make it more green are as follows (8): the replacement of more toxic organic solvents (e.g. acetonitrile) with non-toxic ones such as ethanol or acetone (6, 25), the reduction of the used solvent amount by decreasing the column dimension (especially internal diameter, and length) (26, 27), the application of elevated temperature, and various mobile phase additives such as cyclodextrins, and surfactants (9, 28), the usage of stationary phases that posses shorter alkyl chain (from 1 to 8 carbon) that reduce the retention as well as the application of more polar RP stationary phases (polar embedded) instead of long alkyl chains. Another idea is to use stationary phases based on core-shell particles as an environmentally friendly stationary phase that achieve rapid separations with high efficiencies (29). It allows to reduce the volume of organic solvent usage.

Micro flow HPLC separations as well as ultrahigh performance liquid chromatography (UPLC) with reduced column diameter, reduced column length, reduced particle size, and the application of stationary phases allowing a high water content in the mobile phases are now the most popular alternatives to classical chromatography that allow to reduce the amount of generated harmful solvents waste in liquid chromatography analyses (14, 30–33). Summarizing, traditional RP LC may become an attractive eco-separation technique using typical chemically bonded stationary phases changing the mobile phase conditions, e.g. using ethanol instead of acetonitrile or using novel mixed-mode stationary phases that can operate at highly aqueous mobile phases.

An example of green chromatographic method is the separation of polar compounds, e.g. nucleosides or nucleic bases, in highly aqueous mobile phase. The separation may be done on commercial C18 or C8 stationary phases, however, a phase collapse effect and retention loss may be observed. Other assumption is that separation may be done with the addition of surfactant to pure water or by performing the procedure in elevated or subcritical temperature (9, 10, 28).

Thus, the goal of the research was to test novel stationary phases according their ability to operation in purely aqueous mobile phases at normal temperature without any additives to the mobile phase. Tested materials were characterized and described in the literature (33–35). In the present study, a further characteristic of the selected materials were performed. Four materials, N,O-dialkylphosphoramidate stationary phase and three ester-bonded phases were applied for successful purely aqueous separation of nucleosides, nucleic bases and purine alkaloids.

2. Experimental

2.1. Materials and reagents

The object of the study was innovative stationary phases with polar embedded group (phosphoester or ester): N, O-dialkylphosphoramide stationary phase (Amino-P-C18) described elsewhere (33, 34), and ester bonded phases (Diol-Ester C18, Diol-Ester C10, Diol-Ester Phenyl) (36). Detailed information about stationary phases are listed in Table 1. Column dimension was 125 × 4.6 mm. The structures of the stationary phases used in the study are presented in Figure 1. As a support for the stationary phase synthesis, Kromasil 100 silica gel was used with a particle size of 5 μm, and pore diameter of 100 Å. The detailed procedure of the synthesis was described in the previous works (33, 34). The characterization of surface properties was also provided in the previous studies (33, 34).

![Figure 1. Stationary phases used in the study: A – Amino-P-C18, B – Diol-Ester C10, C – Diol-Ester C18, and D – Diol-Ester Phenyl.](image-url)
Water used as a mobile phase was purified using a Milli-Q system (Millipore, El Paso, TX, USA) in our laboratory. Standards of nucleosides, nucleic bases and purine alkaloids were obtained from Sigma-Aldrich (St. Louis, MO, USA). Detailed data of the compounds used is listed in Table 2.

2.2. Equipment

Experiments were carried out on a Shimadzu Prominence system (Tokyo, Japan), which includes a quaternary-solvent delivery system (LC-20AD), an autosampler (SIL-20A), a column thermostat (CTO-10 AS VP), a spectrophotometric diode-array UV-Vis detector (SPD-M20A), a refractive index detector (RID-20A), and a data acquisition station, as well as on Shimadzu Nexera system (Tokyo, Japan), which includes a binary solvent delivery system (LC-30AD), an autosampler (SIL-30AC), a column thermostat (CTO-30AC), a spectrophotometric diode-array UV-Vis detector (SPD-M20A), and data acquisition station. The data was collected in LabSolutions software.

2.3. Methods

Excess isotherms measurements were done using a minor disturbance method (37–41). Each column was equilibrated with mobile phase of decreasing concentration of organic solvent in water (100, 98, 96, 94, 92, 90, 80, 70, 60, 50, 40, 30, 20, 10, 8, 6, 4, 2, 0) by pumping at least 30 ml of solvent mixture. Perturbation of the base line was done by a small injection (0, 1 – 1 µl) of the mixture with a higher concentration of one solvent than the plateau concentration. The signal was detected with an RI detector.

The thermodynamic void volume of the column was obtained by integrating the retention times of the perturbation peaks over the mobile phase composition (37):

$$V_M = \frac{1}{C_{\text{max}}} \int_0^{C_{\text{max}}} V_R(C) dC,$$

where $V_M$ is the thermodynamic void volume of the column, $V_R$ is the retention volume of the perturbation peak, and $C$ is the concentration of the analyte [mol/L].

The excess isotherm of the preferentially adsorbed solvent from its solution per chromatographic column was calculated with the following equation (37):

$$\Gamma(C) = \int_0^C (V_R(C) - V_M) dC,$$

where $\Gamma$ is the excess adsorbed amount of the solvent in the column.

Chromatographic separations were carried out at the flow rate set at 1 mL/min. The temperature of measurements was set at 30°C. UV detection was performed at 254 nm. The column void volume was determined as a retention time of thiourea (using mobile phase consisting of 50:50 MeOH/H$_2$O) according to (42, 43), that do not exhibit retention in the reversed phase mode and using minor disturbance method.

3. Results and discussion

The stationary phases used in the study contain various functional groups, polar and hydrophobic ones. Such composition offers specific surface properties. First of all, such structures allow their solvation in a wide range of mobile phase composition, in both water-rich and organic-rich mobile phases. Hydroxyl, phosphate and ester groups are capable of hydrogen bond creation, which makes these materials stable in purely water mobile phase. This is the first requirement that has to be

| Number | Substance | Molecular weight [g/mol] | Log $P$ | Dipole moment [D] | pKa |
|--------|-----------|--------------------------|------|----------|----|
| Nucleo bases | | | | | |
| 1B | Uracil | 112 | −0.86 | 1.76 | 9.77 |
| 2B | Thymine | 126 | −0.46 | 4.11 | 10.02 |
| 3B | Guanine | 151 | −0.59 | 5.50 | 8.95 |
| 4B | Cytosine | 111 | −1.10 | 7.00 | 9.83 |
| 5B | Adenine | 135 | −0.57 | 3.85 | 10.29 |
| Nucleosides | | | | | |
| 1N | Uridine | 244 | −2.40 | 5.01 | 9.70 |
| 2N | Guanosine | 283 | −2.70 | >7.0 | 10.16 |
| 3N | 1-methylinosine | 282 | −2.30 | 12.45 |
| 4N | Thymidine | 242 | −1.40 | 5.25 | 9.96 |
| 5N | 1-methylguanosine | 297 | −2.50 | 12.45 |
| 6N | N$^2$-methylguanosine | 297 | −1.90 | 7.92 |
| 7N | Adenosine | 267 | −2.10 | 3.20 | 12.45 |
| Alkaloids | | | | | |
| 1A | Caffeine | 194 | −0.24 | 3.80 | 10.4 |
| 2A | Theobromine | 180 | −0.77 | 4.30 | 9.90 |
| 3A | Theophiline | 180 | −0.26 | 3.51 | 8.81 |
fulfilled to apply a stationary phase for separation in purely water conditions. The second requirement is that a given material has to adsorb separated compounds and that adsorption has to be selective. The last requirement that has to be fulfilled is that the water has to be able to elute the adsorbed substances from the chromatographic column. Thus, the surface composition of the stationary bonded phase has to adsorb water molecules at the level that allows to elute substances from the column at a reasonable time, providing retention factors of solutes in the range from 1 to 10.

3.1. Solvation processes

As the first step of the investigations, a series of stationary phases was chosen that combine hydrophobic (alkyl or aryl) and polar groups (hydroxyl, phosphate and ester). The chosen stationary phases that were presented in Figure 1 have been subjected to solvent adsorption measurement. As it was proven in the previous study, excess adsorption isotherms are a useful tool for chemically bonded stationary phase surface characterization. The obtained excess isotherms of water and acetonitrile are presented in Figure 2. Each stationary phase adsorbs preferentially water from acetonitrile solution. The highest water adsorption was measured on Diol-Ester Phenyl stationary phase and the weakest on Amino-P-C18 material. Nevertheless, adsorption of water is significantly higher than adsorption of acetonitrile on all the tested materials. This indicates good wettability of the stationary phase surface in the water despite of the hydrophobic ligands present in the surface. These results confirm that the tested materials may be used in purely aqueous mobile phases. Additionally, higher adsorption of water results in its higher elution strength that allows to elute the solute from the column.

Analyzing Figure 2, one can observe that shapes of excess isotherms of both solvent for Diol-Ester C10 and Diol-Ester C18 are very similar. It may be a result of the analogue structure that contains diol support modified Figure 2. Excess isotherms of acetonitrile and water plotted vs. volume fraction of water on a series of chromatographic columns: A – Amino-P-C18, B – Diol-Ester C10, C – Diol-Ester C18, and D – Diol-Ester Phenyl.
by alkyl chains via ester bond. Differences in chain length (C10 and C18) are compensated by coverage density (see Table 1). Additionally, the maximum excess of water and acetonitrile are comparable, contrary to Amino-P-C18 and Diol-Ester Phenyl stationary phases. On these two stationary phases, the adsorption of water is about four times higher than the adsorption of acetonitrile. Such differences in surface properties should result in selectivity of the separation of various compounds in the purely water mobile phase.

Adsorption of acetonitrile is also an important parameter in stationary phase characteristics. It indicates the presence of hydrophobic groups in the stationary phase surface, which increases the solute retention and modifies the selectivity of the separation. In summary, the tested stationary phases provide adsorption of both hydrophobic acetonitrile and polar water, which indicates the dual character of the surface. Such stationary phases should offer significant retention and the possibility to elute separated compounds from the column using pure water.

3.2. Purely aqueous separation

The elimination of organic solvent from mobile phases in chromatographic separation seems to be the most “green” option of liquid chromatography. In such case, organic solvents are used only during stationary phase synthesis and column preparation. Separations of various polar compounds: nucleic bases, nucleosides and purine alkaloids are presented in Figures 3–5.

As it is shown in Figure 3, the separation of nucleic bases mixture may be easily performed using the tested stationary phases in purely aqueous conditions. However, significant differences are observed between columns. The separation to the base line was obtained on Amino-P-C18 and on the Diol-Ester C18 stationary phase. However, the separation on Diol-Ester C18 stationary phase was much

![Figure 3. Nucleic bases separation on a series of chromatographic columns: A – Amino-P-C18, B – Diol-Ester C10, C – Diol-Ester C18, and D – Diol-Ester Phenyl, compounds: 1B – Uracil, 2B-Thymine, 3B-Guanine, 4B-Cytosine, 5B-Adenine.](image)
shorter. Detailed parameters of these separations are listed in Table 3. A similar result was obtained using another alkyl stationary phase – Diol-Ester C10. In the case of Diol-Ester Phenyl, the order of the retention was changed and selectivity of adenine and cytosine was insufficient. The highest retention was observed on Amino-P-C18 and the lowest on Diol-Ester C10 stationary phases.

The separation of nucleosides mixture is a more difficult task using pure water as a mobile phase. The most suitable chromatographic mode for such separation is HILIC. Purely aqueous separations use the opposite mobile phase and RP-like mechanism. However, the separation of seven nucleosides mixture was possible on Amino-P-C18 and on Diol-Ester C18 (Figure 4). Using Diol-Ester C18 separation is much faster but some compounds are not separated to the baseline. Detailed parameters of separations are listed in Table 4. Diol-Ester C10 and Diol-Ester Phenyl provide lower selectivity and much lower retention and thus they are not able to separate nucleosides in pure water.

It has to be mentioned, that although Amino-P-C18 and Diol-Ester C18 stationary phases are capable of separating nucleosides mixture, the mechanism of the separation is quite different. While comparing Figure 4A and C, it is easy to observe that the retention order of nucleosides changes between columns. It is a result of particular interactions of nucleosides with functional groups presented in the structure of bonded ligands. The main difference in the structure is the presence of amine and phosphate groups in Amino-P-C18 and hydroxyl and carbonyl group in Diol-Ester C18 material.

The results for purine alkaloids are presented in Figure 5. Contrary to the previous separations, the best results were obtained on Diol-Ester Phenyl stationary phase. Detailed parameters of these separations are listed in Table 5. Amino-P-C18 also allows to separate caffeine, theobromine and theophiline, but the retention time is
Figure 5. Purine alkaloids separation on a series of chromatographic columns: A – Amino-P-C18, B – Diol-Ester C10, C – Diol-Ester C18, and D – Diol-Ester Phenyl, compounds: 1A-Caffeine, 2A-Theobromine, 3ATheophiline.

Table 3. Chromatographic parameters for nucleo bases separation.

| Column           | Compound     | k   | α    | Rs   | N*  | As0.5* |
|------------------|--------------|-----|------|------|-----|--------|
| Amino-P-C18      | 1B           | 0.793 |      |      | 3772 | 0.913  |
|                  | 2B           | 2.006 | 2.530| 7.142| 5012 | 0.820  |
|                  | 3B           | 3.701 | 1.845| 5.632| 3904 | 0.867  |
|                  | 4B           | 5.338 | 1.442| 5.088| 6210 | 1.125  |
|                  | 5B           | 16.635| 3.116| 10.447| 4255| 0.977  |
| Diol-Ester C10   | 1B           | 0.216 |      |      | 5736 | 0.905  |
|                  | 2B           | 0.392 | 1.815| 2.379| 5666 | –      |
|                  | 3B           | 0.554 | 1.413| 1.977| 5756 | –      |
|                  | 4B           | 1.240 | 2.238| 5.931| 6000 | 0.887  |
|                  | 5B           | 1.905 | 1.536| 4.030| 4960 | 0.886  |
| Diol-Ester C18   | 1B           | 0.311 |      |      | 7740 | 0.994  |
|                  | 2B           | 0.647 | 2.077| 4.228| 6873 | 0.880  |
|                  | 3B           | 0.896 | 1.386| 2.884| 7717 | 1.012  |
|                  | 4B           | 2.281 | 2.544| 9.444| 8009 | 1.026  |
|                  | 5B           | 4.198 | 1.841| 6.708| 5293 | 1.438  |
| Diol-Ester-Phenyl| 1B           | 0.164 |      |      | 4355 | –      |
|                  | 2B           | 0.337 | 2.053| 2.096| 4199 | –      |
|                  | 3B           | 0.512 | 1.520| 1.832| 4008 | –      |
|                  | 4B           | 2.026 | 3.957| 5.803| 2152 | –      |

*Data calculated by LabSolution Software, where retention factor (k), the selectivity factor (α), the resolution (Rs), number of theoretical plates (N) and asymmetry factor (As).
unreasonably long. Diol-Ester C18 and Diol-Ester C10 are not capable of separating theobromine and theophiline, which differ in the position of methyl groups. Peaks are not separated to the baseline, however, the retention times are significantly different. It suggests, that the increase in the column efficiency (column packing procedure) should resolve this problem due to narrow peaks obtained.

Tested columns exhibit good intra-day and inner-day precision in purely water mobile phase. The intra-day repeatability of retention times was in the range of 1.11–3.13%. The column was not washed with organic solvent between the analyses. The inter-day reproducibility of the retention was in the range of 2.61–3.26%.

Typical C8 and C18 columns may be used with highly aqueous (>90% water) mobile phases in order to retain polar analytes. However, there have been many reports of its anomalous behavior – a retention loss (44–46). These anomalies have most often been attributed to aggregation of the bonded alkyl chains in the presence of highly aqueous mobile phases, making them inaccessible to analytes. In the current study, this effect was not observed. It is in agreement with the literature (47), where no retention losses for bonded phases containing polar functionalities is also observed. It indicates that the incorporation of a polar group in the bonded phase is an effective way to prevent such losses.

In the contrary to tested polar-embedded stationary phases, the Diol material and C18 stationary phases cannot be operated in purely water mobile phase. In the case of Diol stationary phase, it is a result of weak adsorption of solutes caused by high elution strength of water. Opposite situation is observed on C18 material, where it is impossible to elute test compounds in a reasonable time. Thus, only the proper composition of hydrophobic and hydrophilic groups in the structure of

| Column     | Compound | k   | α    | Rs   | N*  | As0.1* |
|------------|----------|-----|------|------|-----|--------|
| Amino-P-C18| 1N       | 0.725 | 4.102 | 11.25 | 6201 | 0.809  |
|            | 4N       | 2.974 | 1.082 | 1.133 | 6181 | 0.812  |
|            | 3N       | 3.216 | 1.230 | 2.908 | 6056 | 0.817  |
|            | 2N       | 4.795 | 1.211 | 2.791 | 5976 | 0.860  |
|            | 5N       | 7.921 | 1.652 | 6.993 | 6373 | 0.983  |
|            | 6N       | 9.230 | 1.165 | 2.450 | 5865 | 0.895  |
| Diol-Ester C10 | 1N | 0.147 | 2.374 | 1.599 | 1810 | –      |
|            | 2N       | 0.350 | 1.117 | 0.265 | 1295 | –      |
|            | 4N       | 0.504 | 1.290 | 0.629 | 1121 | –      |
|            | 3N       | 0.560 | 1.112 | 0.708 | 2740 | –      |
|            | 5N + 6N  | 0.945 | 1.687 | 3.281 | 5170 | 0.759  |
|            | 7N       | 0.304 | 2.802 | 5.818 | 6158 | –      |
| Diol-Ester C18 | 1N   | 0.852 | 1.227 | 1.860 | 6216 | –      |
|            | 2N       | 1.045 | 1.229 | 2.040 | 6037 | –      |
|            | 4N       | 1.285 | 1.202 | 1.309 | 5588 | –      |
|            | 3N       | 1.545 | 1.098 | 1.067 | 5806 | –      |
|            | 5N       | 1.696 | 1.500 | 5.352 | 6410 | 0.811  |
|            | 7N       | 2.680 | 1.752 | 1.284 | 1513 | –      |
| Diol-Ester-Pheny | 1N   | 0.086 | 2.949 | 1.460 | 1882 | –      |
|            | 2N + 4N  | 0.255 | 1.752 | 1.284 | 1513 | –      |
|            | 6N + 5N + 3N | 0.446 | 1.680 | 2.813 | 4196 | 1.195  |

*Data calculated by LabSolution Software, where retention factor (k), the selectivity factor (α), the resolution (Rs), number of theoretical plates (N) and assymetry factor (As).
bonded ligands allows the separation in purely aqueous conditions.

All separations presented in the manuscript may be provided in buffered water. Addition of a buffer to the highly aqueous mobile phase usually improves possibilities of optimizing the separations by adjusting the pH and ionic strength. Using just pure water as the mobile phase not only does not allow for adjusting the separation selectivity to provide the best sample resolution, but the peaks in non-buffered mobile phases often show stronger asymmetry. The addition of buffer could possibly improve the resolution. However, the idea of this study was to present the application of pure water without any additives. The presented results should not be considered as a final method but as a proof that pure water as mobile phase may be used for separation of various compounds. It has to be also mentioned that a similar result should be possible to obtain using commercially available polar embedded stationary phases.

4. Conclusions

The presented data shows that it is possible to separate various compounds using pure water as a mobile phase at normal temperature, however, careful selection of the stationary phase is necessary. Among the four tested phases, it is possible to find one for separation of each group of analytes that offers selective separation in a reasonable time. Differences in solvation properties on particular stationary phases result in various retention times of solutes between columns. Amino-P-C18 and Diol-Ester C18 allow to separate nucleic bases and nucleosides, whereas Diol-Ester Phenyl separates purine alkaloid in purely aqueous conditions.

The presented work should not be considered as a presentation of final methods of the separation of given compounds but as a confirmation that it is possible to perform separation in liquid chromatography using only pure water as a mobile phase and eliminate organic solvent from the mobile phase. The obtained results are similar to traditional RP LC and HILIC methods in terms of separation selectivity. The column packing needs further work to obtain better efficiency but the first step has already been done.

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Disclosure statement

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