Pure water as a mobile phase in liquid chromatography techniques

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Abstract:
Liquid chromatography is a technique that is gaining increasing interest and application, for example in the pharmaceutical industry. At the same time as the increase in the number of analyses performed, the amount of organic waste produced while working with high-performance liquid chromatography (HPLC) apparatus is growing. Therefore, new methods and materials are being searched for to achieve the socalled “green” chromatography. In the following review we describe one of them, specifically the replacement of harmful organic solvents such as acetonitrile, methanol or isopropanol, with pure water used as the sole component of the mobile phase. In order to achieve a single component mobile phase, different methods or materials are used: the use of elevated temperature, the selection of new stationary phases, the utilization of changes in the properties of the stationary phase while using a highly polar eluent.

Keywords: Chromatography, Eluent, Stationary Phases innovation.

Introduction

Organic solvents and hazardous waste productions is a worldwide problem that has influence not only human health but is also dangerous for our environment. Facing this problem, it is obvious that chemical industry including all laboratories, need to introduce new technologies and innovations that allow to reduce the amount of waste production. That awareness brings us to development of “green” chemistry such as high-performance liquid chromatography (HPLC) using nontoxic mobile phases, which has received increased attention. The idea of elimination of huge amount of organic and hazardous waste produced everyday with environmentally friendly water is beneficial both ecologically and economically [1].

Quick, easy and environmentally friendly methods of HPLC separation are sought for. Due to the harmful effects of organic solvents, affecting not only humans, but also the environment, “green” technologies are being developed. Separation techniques, including chromatographic techniques are based on the consumption of large amounts of organic solvents. Thus, interest and demand for research towards the separation of mixtures under environmentally friendly conditions are increasing. There are many ways to make liquid chromatography “green”. These include: decreasing the dimensions of the HPLC column to use smaller flows that reduce the amount of organic waste generated [2]; using mobile phase additives such as cyclodextrins [3] or surfactants; stationary phases with shorter carbon chains [4]; core-shell columns; operating at elevated temperatures [5]; replacing organic solvents with other, more “green” solvents such as water, ethanol or supercritical CO_2 . Among the above-mentioned, separations performed with use pure water as the only eluent in HPLC are the main issue of this paper. For such analyses to be carried out, it is necessary to apply appropriate separation conditions and special columns allowing for selective separation of the substance with such a highly polar solvent [6].

Solvents that are commonly used for reversed phase liquid chromatography, such as acetonitrile, methanol, isopropanol, tetrahydrofuran and additives (i.e. trifluoroacetic acid, which is highly ecotoxic and slowly decompose) are the main product of harmful waste. Considering “green” chromatography they should to be replaced with environmentally friendly alternatives. Therefore, it is important to find HPLC techniques in which the above-mentioned solvents are replaced with less toxic ones, such as ethanol [7] (ethanol is assigned to “green” solvents due to its low toxicity and, possible synthesis from renewable sources, but mainly because its lifecycle has low impact on environment), water [8,9], superheated water [10,11] or liquid carbon dioxide [12]. Reaching totally “green” liquid chromatography which completely eliminates organic solvents, there are only left water and carbon dioxide (supercritical or subcritical) as a mobile phase. This exchange is difficult and need special methods, conditions and equipment. For example, eluotropic strength of water can be increased but elevating temperature, reaching even superheated water [11]. Moreover, using of conventional C18 stationary phase results with phase collapse, when water is used as a mobile phase [6].

Replacement of solvents with less harmful ones is one of the Rs of green analytical chemistry (Reduce, Replace, Recycle). Not only reducing of unwanted risks and harmful solvents, but also total elimination of them can be provided by using this solution of greening separation techniques. Recently there is growing interest in greening principles in laboratory work, where minor changes in procedures multiplied by the number of analyses performed in laboratories around the world, can together give a significant impact [13]. High-performance liquid chromatography is one of the most common analytical techniques. Stationary phase columns used for separation usually has 4.6 mm internal diameter (i.d.), 25 cm length, and work at mobile phase flow rate between 1 and 1.5 ml/min [14]. These conditions lead to daily production of over 1 litter of effluent by each HPLC instrument that has to be utilized as a chemical waste. While this amount of solvent waste seems small in comparison to industrial production, however, the ubiquity of HPLC apparatus makes its significant. It is not uncommon that single pharmaceutical company can operate with over 1000 HPLC apparatus. Adding the fact that automation of this technology provide 24-h operation, cause that problem with waste-care, has to be handle out [13].

Subcritical water as a mobile phase

Term “high-temperature” appear to be not exactly defined. Usually it is explained as “higher than room temperature” or “higher than the boiling point of the solvent of mobile phase” but also definitions like “higher than 100C” or “in range between 40C and 200C” can be found in the literature [15,16]. Interest related with temperature as a key parameter in liquid chromatography is still inconsiderable and does not appear in routine laboratory work. Lack of commercially available equipment, such as column oven, that can reach and maintain high temperature (up to 200°C) and deficiency in thermally stable stationary phases, may be the limits of this technique. Although in last two decades this topic has grown in interest what can be seen in several reviews that have been published [10,11,15-21]. Large spectrum of the physicochemical parameters affected by the temperature may discourage the analysts. Only influence of temperature on the decrease of viscosity of mobile phase is often mentioned. Other important effects such as decrease of eluent strength, increase in diffusivity and change in selectivity and dissociation rate of ionizable compounds are often not considered. This provides to change of conclusions regarding the manipulation of this parameter, from the fact that real benefits and restrictions of high-temperature analysis are not consider entirely [16].

The change of analysis temperature can replace the change of concentration of organic solvent in mobile phase or eliminate it at all. It can be found that temperature change may have similar effect to change in the solvent concentration. Bowermaster and McNair [22] found that change of 1% in methanol concentration is equivalent to change temperature for 3.75°C. Chen and Horvath [23] found similar effect with acetonitrile. The increase of 1% ACN (acetonitrile) corresponds to temperature increase of 5°C. Similar results were obtained by Tran et al. [24]. Kondo and Yang [25] conducted series of experiments that proved temperature change correspond to change of given organic solvent concentration depends on conditions and column that has been used. For example, 3.5°C rise in temperature is equivalent to approximately 1% increase of methanol concentration in methanol-water mobile phase when polystyrene-divinylbenzene (Hamilton PRP-1) column was used. Temperature change between 5°C and 8°C was similar while change concentration of acetonitrile by 1% in acetonitrile-water mixture was performed. However, usage of Zorbax RX-C18 column give results of 1% increase of methanol concentration equivalent to 2°C rise of the temperature, while same change in acetonitrile concentration is equivalent to 3C rise of the temperature. The retention time of three compounds: pyrogallol, resorcinol and catechol were compared in above mentioned experiment [25].

Depending on the conditions used, this technique can be named as “Subcritical water chromatography” (SBWC), “Chromatography in very hot water” “Superheated Water Chromatography” (SHWC) [16], “High Temperature Liquid Chromatography” (HTLC) [18,26] or “Pressurized Hot Water Liquid Chromatography” (PHW-LC) [27]. Pure water in elevated temperature can be used as mobile phase in liquid chromatography mainly due to change of dielectric constant. Water dielectric constant is reduced from 85 at 25°C to 35 at 200°C cause that water behave like an organic solvent. Because of that, water can became an extremely effective solvent for low-polarity, organic substances, such us organic pollutants [28]. This allows to conduct experiments in completely “green” conditions for thermally stable solutes and stationary phases [15].

Water in the conditions below critical point, that is 374°C and 218 atm., is considered as subcritical water (Fig. 1). Another terminology for water in these conditions is: superheated water, hottemperature water, pressurized hot water. In ambient conditions water is too polar to be efficient eluent in chromatographic analysis. However, with increase of temperature it can be observed dramatically decrease of water polarity. Such high critical point of water allows wide spectrum of temperature and pressure values to choose. Therefore, such unique characteristic of subcritical water provides widely tunable parameters such as dielectric constant, surface tension and viscosity, which decrease with increase of water temperature (Fig. 2). However, this does not mean that solvents are optimized for a single parameter, e.g. a dielectric constant, as this single parameter does not affect either the selectivity or the elution strength. It is necessary to take into account all changing parameters with a change in the temperature of the mobile phase, as well as their tendency to change e increase or decrease. Pressure has low influence on those above-mentioned parameters, as long as water remains in liquid phase. Thus, subcritical water can imitate traditional RP (reversed phase) separations with organic solvents as modifiers in mobile phase. Additionally, dissociation constant increases by three orders of magnitude when temperature is elevated from 25ºC to 250ºC. Further increase of temperature causes decrease in constant. It means that water in high temperature acts as both stronger acid and stronger base compared to water in ambient temperature [10].

Although full range of applications and possibilities has not been recognized for SBWC, this technique should work for substances in the full spectrum of polarity. At low temperatures of analysis this technique works for polar compounds, moderately polar substances in mild temperatures and for non-polar substances in high temperatures, if stationary phase is stable in that range of temperature. This division is related to the influence of temperature on the adsorption of the analyte. Analytes adsorption is reduced with the temperature increase but this change is dependent on their polarity. At the same time, the viscosity of water is also reduced. Lower viscosity of mobile phase causes by elevated temperature gives low backpressure that allows SBWC separation to be performed with much higher flow rate. Thanks to that, shorten separations times can be achieved, analytes will be less exposed to high temperature, so it will minimize the analytes degradation.

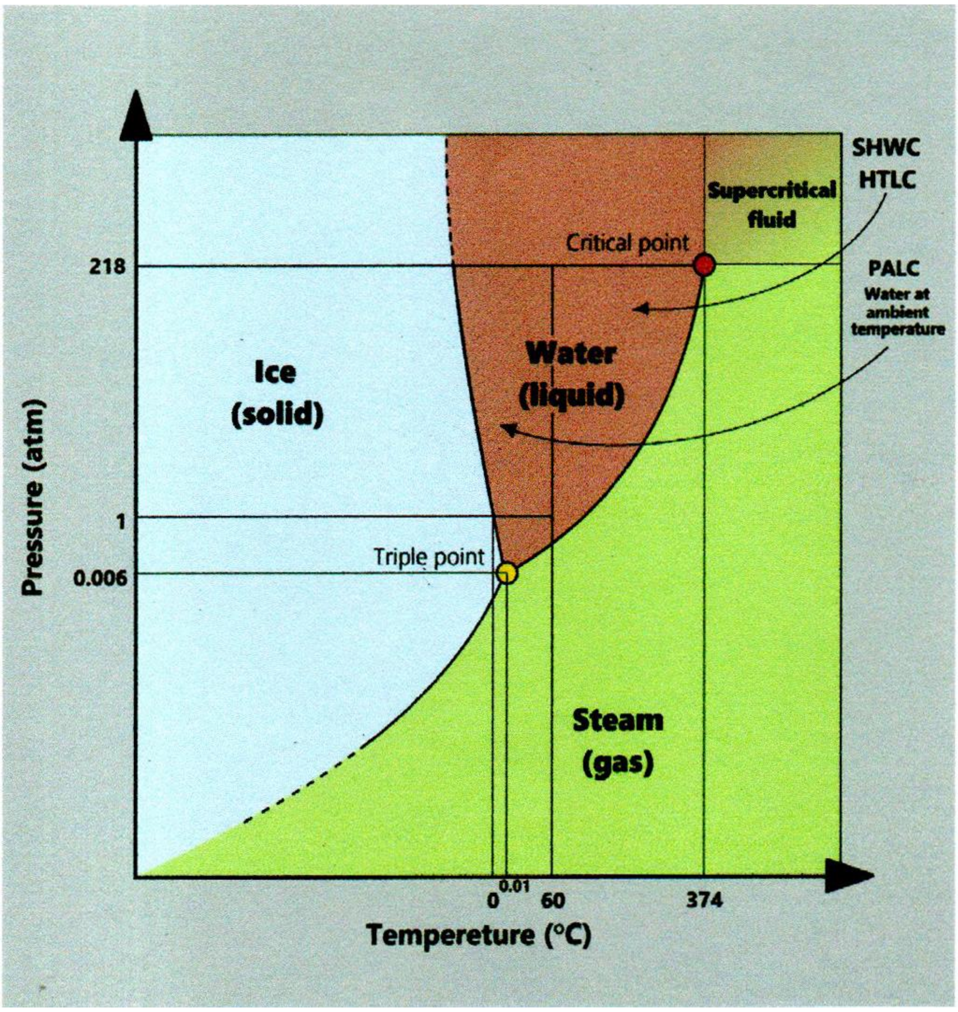

Fig. 1. Schematic water phase diagram. Below the critical point, that is 374 K and 218 atm., the water is in the liquid state and is termed subcritical water, hot-temperature water, pressurized hot water [10].

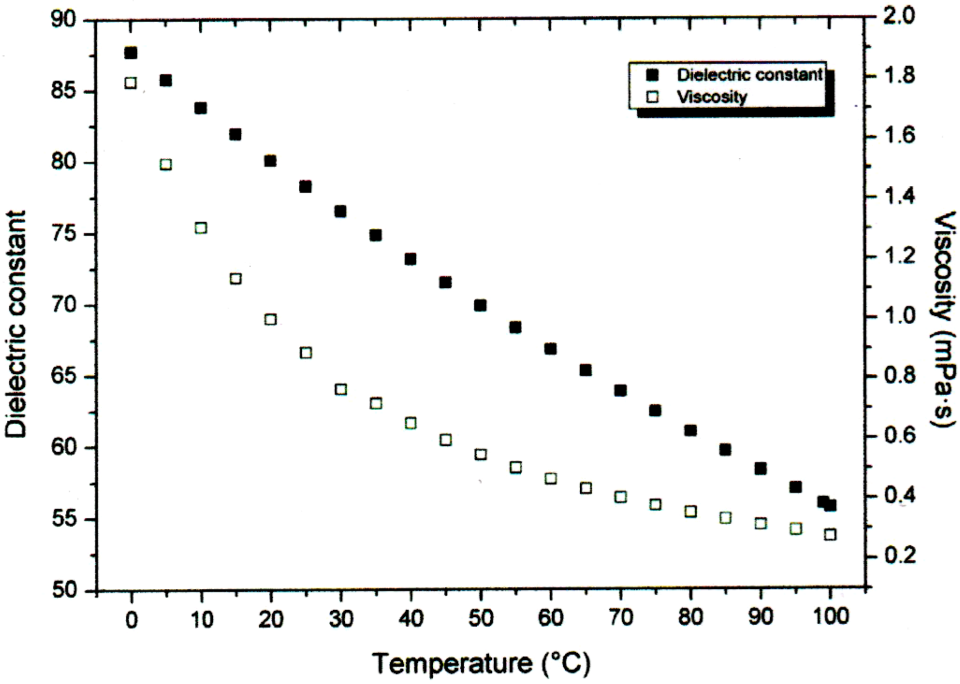

Fig. 2. Changes in dielectric constant [168] and viscosity [169] of water in the temperature range 0–100°C

Therefore, degradation of analytes is not major problem using separation techniques in SBWC for low molecular weight substances [10].

First reported separation with use of subcritical water as a mobile phase was conducted by Smith and Burgess [29]. Experiment was carried out with superheated water up to 210°C to separate number of phenols, parabens and barbiturates on a polystyrene-divinylbenzene (PS-DVB) column. They showed that retention factors systematically decrease with increase of the temperature. Also, there was performed comparison of superheated water separation with conventional reverse-phase conditions. As approximately equivalent to 180°C water the 20:80 acetonitrileewater mixture was used. Separations were performed to show that superheated water can be used to resolve analytes which are characterize by wide range of hydrophobicity.

To separate more hydrophobic propyl and butyl esters a higher temperature of 210°C was required. The oxidization and degradation of solutes or column was not observed as well as hydrolysis of ester functional group. Under these conditions the low back pressure of about 15 bars was noticed, as the vapor pressure of water is relatively low. As a conclusion authors report that comparison of conventional reversed-phase chromatography using water organic eluent and use of superheated water as mobile phase, showed that SHWC have enhanced separation and even shorter analysis time [29].

Application of subcritical water chromatography

For chromatographic analysis conducted at elevated temperatures, one of the concerns is the instability or degradation of the analyzed compounds. Considering water as a mobile phase, the two most likely reactions are hydrolysis and oxidation[11]. Due to the higher temperature of the chromatographic analysis, the viscosity of the water is reduced and the backpressure is low. This allows a higher mobile phase flow rate to be used. By combining high temperature and high flow rate, the analysis time is shortened. Therefore, SBWC analyses cause less exposure of the sample to hot water, resulting in no degradation of the analytes [10]. With an analysis time of between 5 and 30 min and an elevated temperature, a typical chemical reaction includes dehydration. However, dehydration will not occur due to the entirely aqueous conditions of the separation. The oxidation reaction will also not occur due to the prior degassing of the sample and the mobile phase, or by flushing with nitrogen to avoid rusting of the metal parts of the apparatus [11]. Taking parabens as an example, the alkyl p-hydroxybenzoates can be expected to undergo oxidation or hydrolysis reactions. However, Smith and Burgess [29] demonstrated that even under analysis conditions up to 200°C these compounds are thermally stable and no degradation has been observed. It has also been reported that some pharmaceutical compounds will not decompose when using fast LC (liquid chromatography) analysis. Reduced analysis time results in lower exposure of analytes to the reaction occurring on the column. Thompson and Carr analyzed a number of drugs and alkaloids to determine their thermal stability. They found that using reversed phase liquid chromatography, the stability of the studied compounds is related to the rate of their degradation under ambient conditions and the residence time in the column. Only norpseudoephedrine showed significant degradation. Therefore, it was found that many complex compounds can be determined at high temperatures [11,30]. It is therefore claimed that degradation of analytes is not a major problem during SHWC analyses with most low molecular weight compounds [10].

Several other cases where degradation took a place have also been reported. Thiamine can be analyzed up to 50°C, while at 160°C it breaks down to form a range of degradation products determined by on-line mass-spectrometry (MS) and nuclear magnetic resonance (NMR) spectroscopy [31]. Nitrobenzene was tested at temperatures above 220°C on the polystyrene divinylbenzene column, where it was degraded. At lower temperatures and with the use of a less retentive column, it showed stability [11]. Research on polycyclic aromatic hydrocarbons in the temperature range from 100°C to 350°C and heating time from 10 to 240 min in pressurized hot water was aimed at demonstrating possible degradation. Most of the compounds disintegrated in a short time of 10 min at a temperature above 300C. In some cases the losses were observed already at the temperature of 100°C [32].

As mentioned above, SHWC should work for substances with full range of polarity, mainly due to decrease of water viscosity and polarity with increase of analysis temperature. A wide number of low molecular weight compounds has been already separated with use of superheated water chromatography including alcohols[28,33–38], aldehydes [39], aliphatic aromatic ketones [40] alkanols [26,33,35,41–44], alkyl benzenes/chlorinated benzenes/benzene derivatives [34,37,45–51], amino acids [52–54], anilines [25,45,54,55], aromatic acids [40], aromatic hydrocarbons [56], aromatic standards and alkyl aryl ketones [40,57,58], barbiturates [29,59,60], benzoates [61], caffeine derivatives [28,46,62,63], carbohydrates [52–54,61,64], carboxylic acids [52,65], chlorinated hydrocarbons [38], chlorophenols [66], diethyl phthalates [48,61], flavones [67], model drugs [68–72], nucleobases [61], parabens [29,59,61,63,73], phenols [25,28,29,38,45,47,54,55,65,70,74–76], phosphonic acids [53], polychlorinated biphenyls (PCBs) [77], polycyclic aromatic hydrocarbons (PAHs) [47,61,77], polyethylene glycols [78], polyhydroxybenzenes [25], PTHeamino acids [79–81], pyridines [25,55], steroids [80,82–84], sulphonamides [85,86], triazine herbicides [87], triazole fungicides [88] and water-soluble vitamins [31].

SHWC instrumentation

The application of the SHWC technique requires the use of suitably adapted apparatus. Additional elements need to be inserted in the conventional HPLC instruments. Although the standard HPLC apparatus has a heating oven, the temperature range does not exceed 80–100°C. In addition, such a heating system does not maintain a constant temperature in the column during the analysis [10,11].

Carr and coworkers developed a high-temperature ultra-fast LC apparatus that uses additional pumps to eliminate thermal mismatch, and avoid band broadening by using a separate pump that allows direct injection of the analyte into the column [76]. Most of the systems operating in SHWC are based on GC ovens, which have the ability to heat up to 350°C, and temperature programming. However, there is a problem with the delay in achieving thermal equilibrium between the oven and the column. In hightemperature chromatography it is important to ensure fast heating of the column. Tautenberg and co-workers [82] developed a special oven that allows for fast heating of the column up to 225°C and efficient cooling with circulating oil, which reduces the cycle time. Another way to avoid such a problem is the idea of direct heating of the column by wrapping it with resistively heated wire was developed, which allows for more rapid and repeatable heating of the column than in the case of common heating methods [33]. Currently, there are several column ovens available on the market, which allow to heat up to 200°C in both isocratic and temperature gradient conditions. The ovens have three separately controlled heating zones, pre-heating, column heating and cooling system. Another emerging problem is the creation of back pressure at the output of the column to prevent water from boiling. One of the solutions is to use a simple length of PEEK tube with a narrow diameter (typically 3 m 0.13 mm I.D.), which may be sufficient at a flow rate of 1 ml/min [11].

During the injection, there is a problem with the preparation of the sample. If the sample is water-soluble, the injection will be normal. However, if the solubility of the analyte in water is low, an organic solvent may be used to allow for homogeneous sample preparation, if the solvent has a higher retention rate than the analyte. The problem of band broadening due to the presence of organic solvent is avoided [89].

Due to the temperature difference between the mobile phase and the chromatographic column, there is a problem with the thermal mass entering the column, which can cause an unwanted cooling effect. In the SHWC, it is therefore important to use preheating in the form of a coil inside the oven or heating on an inlet line. This problem is more severe when using high flow rates of the mobile phase. It is therefore suggested that the temperature difference between the mobile phase and the column should not exceed 5°C. Also the length of the preheating coil must be adjusted to the flow rate and parameters of the column. Fields and coworkers [90] investigated that a 15 cm long coil with an internal volume of 3.4 ml yields distorted peaks at flow rates above 0.7 ml/ min. However, in the same conditions, when using a 140 cm long coil, good peak shapes were maintained even up to a flow of 1.5 ml/ min. Using a metal block in close contact with the inlet tube, causes heat transfer allowing the use of a relatively short tube, 15 cm long, sufficient up to 190°C [11,82,91].

Packing materials in SHWC

When considering analyses carried out with water in a subcritical state, it is important to pay attention to the thermal stability of the stationary phases. Most of the columns stable under ambient HPLC analysis may show instability under superheated water conditions. In both, ambient temperature HPLC and SHWC, there can be seen a linear van't Hoff relationship between retention factor (k) and inverse of absolute temperature (1/T) [57,69]. One of the main examples is the commercially available octadecylsilane (ODS) silica material for column packing, which undergoes degradation in conditions above 80°C [11]. Therefore, there is a demand to search for new materials or modify them in order to find a thermally stable column packing in the SHWC. The elevated temperature lowers the polarity and surface tension of the water, so that superheated water can be used for the separation of both polar and non-polar compounds. Studies on interactions between analytes in superheated water and the normal-phase and reversedphase packing materials have been studied by Yang et al. [92]. They concluded that the energy, and therefore the temperature needed to elute the compounds when using the reversed phase columns, is higher than when using the normal phase columns. In addition, the presence of aromatic interactions increased this differentiation.

Analyses carried out with ODS silica gel allowed us to observe the phenomenon that occurs at the water concentration in the mobile phase of over 95%. In such conditions a sudden decrease in retention times occurs while maintaining efficiency. It was found that this effect occurred when the columns were not used for some time and were not under pressure. This phenomenon was attributed to the so-called “phase collapse” [93]. It consists in the laying of long, hydrophobic hydrocarbon chains C18, which reduces the adsorption available surface of the stationary phase. Therefore, an attempt was made to eliminate this effect. For this purpose, polar groups between the connections of hydrophobic chains C18 with the surface of silica were incorporated. This allowed to obtain a mixed hydrophilic-hydrophobic phase with simultaneous improvement of its wettability. Such phases were named after polar-endcapped phases, polar-embedded phases or aqueous phases [94,95]. Changes in retention using SHWC analysis were observed for columns with built-in polar groups, especially when they cooled down and left without flow for a period of time. The ‘phase collapse’ process is reversible using an eluent with a high content of organic solvent. However, the occurrence of this effect occurs suddenly, even between analyses. The behavior of stationary phases in high aqueous eluent has been described by Walter et al. [96], where attempts were made to predict the above mentioned effects. Currently, the effect of “phase collapse” is explained by the phenomenon of de-wetting of the phase surface, which reduces the effective volume of the column by removing water molecules from the pores [97].

The lack of stability of commercial silica columns with attached octadecyl groups forced the search for new column packings that are stable in superheated water. Currently, in SHWC and other chromatographic analyses using high percentage of water in the mobile phase, modified silica phases, polymer phases, zirconiabased and other metal oxides phases, carbon phases and hybrid phases are used [10,11].

Silica-based packing materials

Conventional silica columns are used in water conditions. However, their lifetime and the temperature range in which they can operate is low. Most of the C18 phases have a low lifetime, although they are used in SHWC analyses [68]. The most common columns with silica filling include Nucleosil C18 AB [45,62], Zorbax[69], Zorbax RX-C8 [62], Zorbax RX-C-18 [25,98], Xterra [68,69,84], Xterra RP 18[99], Gemini [69], Kromasil-C18 [46], Luna C18 [100] and many more, see Yang [10]. Typical temperature range for silica-based columns is from 50°C up to 150°C. With a small addition of an organic modifier this range can be slightly increased to 200°C, although the recommended range with 100% water is up to 100°C, for the same column material [101].

Polymer-based packing materials

Polymeric phases are commonly used in elevated temperature chromatography, e.g. for size exclusion chromatography. Because of that they are expected to be the most thermally stable material for analysis with superheated water as a mobile phase. The most commonly used columns with polymer filling for use in SHWC include polystyrene divinylbenzene column PLRP-S (PS-DVB) [29,31,46,59,63,68,85,86] and filling with crosslinking polymer PRP-1 [25,28,33,39,52,54,102]. Thermal stability of these columns is in the range from 100°C to 200°C. There are even works with new polymers containing amino acid, which are suitable to work under superheated water conditions up to 150°C for 500 h [103]. However, in comparison to columns filled with silica, they have a lower column efficiency, which may result from the high retention capacity, which causes that elution of moderately polar compounds, such as alkyl aryl ketones, can be achieved only at high temperature.

Zirconia-based packing materials

Thermal instability of silica phases directed the researchers in search of matrices built of oxides of other metals, such as alumina, zirconia or titania oxides. A wide reviews of this compounds used in chromatography were prepared by Nawrocki et al. [104–106]. Zirconia-based materials for chromatographic column packings were first developed by Carr and co-workers [104,107]. However, problems arose during modification of the surface of amphoteric oxides with alkyl carbon chains. This required the use of mobile phase additives in the form of e.g. fluoride ions. Finally, it turned out that only zirconium compounds are used as effective materials for the preparation of chromatographic columns. The most commonly used are encapsulated zirconia by polybutadiene (PDB) known as ZirChrom-PDB [43,46,48,49,67,68,82,88,90,108] and by polystyrene (PS) e ZirChrom-PS [62,67,76]. There are also other zirconia-based materials such as carbon coated zirconia (CARB) e ZirChrom-CARB [49,68,100] or secondary bonded C18 zirconia column (Diamondbond) e.g. ZirChrom-DB-C18 [46]. Thermal stability of PDB columns has been determined at 200ºC. However, manufacturers recommend using it up to the upper limit of 150ºC. Wu et al. [43] discovered that the stability of the PDB column in the recommended conditions is about 200 h, while the upper limit of temperature at which it can actually be used is about 260ºC. Kephart et al. [49] showed that capillary PDB and CARB columns are stable up to 370ºC and 300ºC respectively at the pressure of about 758 bars. They were successfully used for separation of phenol compounds and alkylbenzenes.

Carbon-based packing materials

Carbon based packing materials for chromatographic column were investigated mainly due to its high thermal stability. For this reason, porous graphitized carbon (PGC) was used [109–111]. However, large activity of carbon materials caused that contamination problems appeared, what conclude in problem with asymmetric peak shapes. Even with such high-thermal stability, PGC column efficiency declined with a time, due to difference in thermal expansion of carbon and stainless-steel column material. This resulted in a mechanical stress through which the column loses its separative properties [87].

Detectors applied in superheated water chromatography

Detectors used in conventional liquid chromatography techniques are dependent on the composition of the mobile phase, in particular the organic modifier concentration. Thus, the detection used in liquid chromatography was dominated by UVeVis and fluorescence spectroscopy as well as by refractive index detection, mainly due to the small influence of the matrix composition changes on the quality of the determinations. In addition, the high availability, versatility and low cost of UV detection, have led to their use even in analyses using superheated water. However, the use of 100% water as a mobile phase has opened up the possibility to use other, more universal methods for the determination of analytes. These techniques include Flame Ionization Detector (FID), Mass Spectrometry (MS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Nuclear Magnetic Resonance (NMR), Evaporative Light Scattering Detection (ELSD) and others like amperometric detector or Fourier Transform Infrared Spectroscopy (FTIR) [10,11,18] (Fig. 3).

Using a UV/visible absorption technique, using pure water as the only eluent component has the advantage of no background peaks from organic solvent. This type of liquid chromatography uses a thermal gradient instead of a concentration gradient, making available techniques where an organic modifier causes detection difficulties, e.g. by changing the volatility of the mobile phase and the analytes. Also, it offers the possibility of determination of analytes at short wavelengths, even below 200 nm. Yarita et al. [78] showed that this technique is suitable for determination of low molecular weight polyethylene glycols at wavelength of 190 nm. The use of wavelengths below 200 nm allows for increased sensitivity only for clean samples. Determination of real samples involves limitations due to the presence of matrix compounds that strongly absorb high energy radiation, resulting in the hiding of analytes' peaks [18]. However, there are also other restrictions related to the use of hot water. Due to the use of elevated temperatures, the back-pressure has to be controlled for keeping water at liquid state, so the flow cell of the detector should be able to withstand this pressure [11]. For this reason, a back-pressure regulator or resistor should be placed at the outlet of the UV/Vis detector. Most of UV/Vis detectors are not adapted to use in high temperature, therefore the cooling system has to be applied to introduce liquid analysis at ambient temperature. Decreasing of temperature cause increase of polarity of aqueous mobile phase, thus deposition of moderately and nonpolar analytes in transfer tubes can appear [10]. It can be seen that UV/Vis technique, when elevated temperature is applies, losses its universal application, mainly due to appearance of above-mentioned drawbacks.

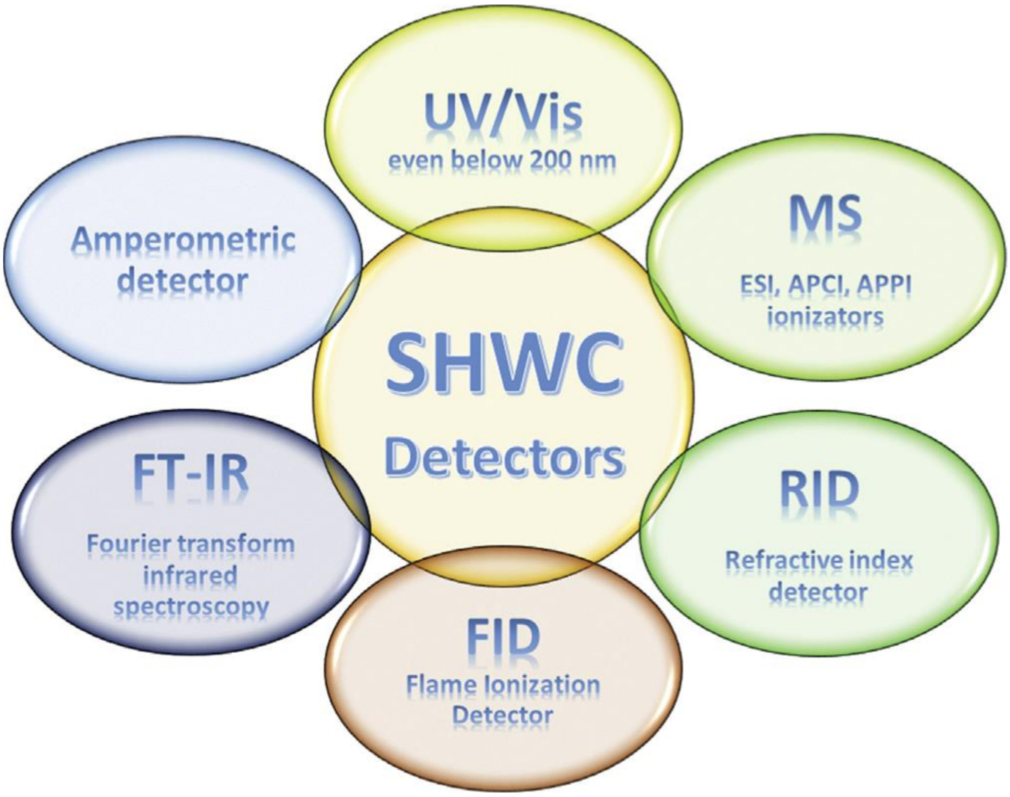

Fig. 3. Diagram illustrating the wide detection spectrum possible through the use of pure water in superheated water chromatography (SHWC) [10,11,18].

The flame ionization detector is a sensitive and universally used detector in gas chromatography. Due to the lack of such a sensitive apparatus in LC techniques, attempts have been made to use it for liquid phase determination. It is well known that the FID is used for non-volatile analytes and for the determination of all substances containing carbon, which makes it a very versatile detector. Unfortunately, the widespread use of organic solvents in both normal and reversed phase systems in LC increases the volatility of the analytes and provides a significant background for FID-based determinations. Water is transparent for FID, so the use of 100% water as a mobile phase increases the possibility of using FID in liquid chromatography determinations. However, pure water at room temperature is not a good eluent for all columns and compounds in LC. For analytes that can be separated at ambient temperature in pure water, Synovec et al. [37,38] have developed a FID for the determination of alcohols and hydrocarbons. Krejcí and coworkers[112] performed first determination using capillary column LC online coupled with modified FID with usage of 100% water as eluent. In later years many FID modifications for liquid chromatography determinations were carried out, but all of them required the elimination of organic modifiers from the mobile phase [37,38,53]. An unmodified FID was used by Miller and Hawthorne [42] to determine groups of polar organic compounds using the SHWC. They concluded that placing the end of the capillary resistor placed at the output of the column at a level below 3 cm from the tip of the FID gave results in which the detector signals were the most stable. These results were also confirmed in later works [36,39,52,54]. Such placement of the resistor allowed to keep the water in liquid state even at temperatures above 100^{o}C. Also thermal gradient was investigated as part of their studies [42].

Mass spectrometry is one of the few detection techniques which, in addition to information on the presence of a product, is able to determine what is the product. The use of MS detection in liquid chromatography requires an ionization technique that allows the liquid to be ionized. The most common techniques are electrospray ionization (ESI) [113e115], atmospheric pressure chemical ionization (APCI) [116–118] and atmospheric pressure photoionization (APPI) [119]. The possibility of coupling MS detection with liquid chromatography gives the possibility to use it also using techniques such as SHWC. The effectiveness of coupling to the MS detector is related to the processes of nebulization, evaporation and desolvatation. As a consequence, the different compositions of the mobile phase in the LC, and therefore its different properties such as surface tension, polarity and viscosity, influence the detection results. Therefore, there are few applications in the combination of APCI-MS detector and HTLC [120]. This is due to the low sensitivity and mass dependence of this type of ionization. The ESI ionizer, which was used in temperature programming, enjoys a higher sensitivity compared to the concentration gradient, as a result of the faster evaporation of the hot moving phase, which reduces noise [121–123].

Although NMR detection is much less sensitive than other analytical methods, the fact that it is non-destructive for the analyte causes a growing interest in it as a detector to LC. Applying NMR analysis to conventional LC coupling requires the use of suitable deuterated solvents such as methanol and acetonitrile, which are expensive. This is necessary due to the presence of too large background signals from protons of non-deuterated solvents. The use of HTLC coupling with NMR detection is therefore beneficial. Deuterated water is easily available in high purity and at an affordable price [18]. NMR spectra have significantly less interference from the mobile phase with clean water than with conventional solvents. In addition, there is a possibility of coupling NMRMS detection, which allows to simultaneously obtain the spectrum of both 2D and 3D [70]. SWHC-NMR-MS was used to analyze barbiturates [60], drugs [70], sulfonamides [86] and ginger extract [99]. PS-DVB polymer columns [31,60,70,71,84,99] were mainly used, but ODS columns [99] were not excluded, which are characterized by lower thermal stability

Among other noteworthy detection methods one can distinguish refractive index detection (RID), amperometric detection or Fourier transform infrared spectroscopy (FTIR). The main problem with the use of these techniques is the change in the baseline resulting from the concentration gradient used in conventional LC methods. However, an alternative to this gradient may be temperature programming, which is used in the SHWC. The instability of the base line and the presence of high noise levels compared to other methods is a feature of RID. The use of a single-component mobile phase in SHWC allows to reduce these effects. The temperature change of course influences the physicochemical properties of the eluent, which is also reflected on the detector base line, however, this can be corrected by appropriate software. It has been proven that the use of high mobile phase flows and good cooling of the eluent before entering into the refractive index detector system allows the detection results to be obtained without loss of sensitivity using a temperature gradient [124,125]. Amperometric detector was successfully used for temperature programmed analyses with electrochemically active compounds. The drifts of baseline were eliminated by simple mathematical approach. There were no evidence of influence of temperature gradient on retention nor sensitivity [126]. The coupling LC-MS has a drawback that do not distinguish between isomers. Therefore, the combination of these techniques with infrared spectroscopy will allow full separation and analysis of mixtures. Also, in this case the use of a temperature gradient is more advantageous in relation to the composition gradient. The HTLC coupling with FTIR was performed by Greibrokk et al., where this technique was used to separate complex antioxidants [127].

Per aqueous liquid chromatography (PALC)

As mentioned above, the elimination of organic modifiers from the mobile phase in the LC makes only water and CO_2 in the sub- or supercritical condition are the only two fluidic media that can be used as a fully “green” solvent. Considering the water, which is the subject of this review work, temperature control allows for changes in the eluotropic strength of water [128]. However, there are still doubts about the stability of both the columns and the solutes at high temperature. Hydrophilic Chromatography (HILIC) allows the separation of mainly polar compounds. Currently the most common solvent in HILIC analyses is ACN. The influence of water presence in the mobile phase on silica hydride columns using aqueous normal phase (ANP) technique, has been pioneeringly described by Pesek et al. [129,130]. Bimodal curves form 0e100% water concentration were performed to determinate the changes in retention for separation of epiribicin and analogs, as well as to investigate the mobile phase layer rich in water associated with the surface of silica [131,132]. Bidlingmeyer studies were the first in which pure silica was used to separate amines in HILIC and also the mobile phase with high water content was studied [133]. They have proven that with high water content, the surface of silica becomes non-polar. Siloxane groups contribute to the hydrophobic character of silica [134]. The hydrophilic character is assigned to free silanols, which, depending on the pH, may have an ionic nature.

The use of pure water makes polar silica in HILIC adopt a nonpolar character. The use of the term reversed HILIC suggests that the RP-LC technique is used. Therefore, A. dos Santos Pereira et al. introduced a new name, per aqueous liquid chromatography (PALC) to distinguish this method from HILIC, RP-LC and ANP LC (aqueous normal phase LC) [135]. A schematic illustration of the mobile phase and the stationary phase used in PALC is shown in Fig. 4. At first, they used the two coupled Zorbax-Rx-SIL columns for the determination of underivatized amino acids in biological liquids. The plot of retention times in function of ACN concentration was determined. It showed that after a dip related with decreasing of ACN content, there can be observed an increase of retention times with major changes in selectivity. They also demonstrated that the separation of catecholamines, which failed in standard HILIC on superficially porous particles [136], was successfully carried out using PALC with excellent peak shapes and high efficiency. In later works aimed at developing a description of the PALC technique, Gritti and A. dos Santos Pereira explain the mechanism of retention and the effect of the use of the water-rich mobile phase on efficiency [137,138]. The adsorption mechanisms were explained by the adsorption isotherms measured by frontal analysis (FA) on core-shell particles of neat porous silica (Halo) column package.

The major differences between PALC and HILIC adsorption mechanisms were proven. In both, water-rich and acetonitrile-rich conditions, retention factors were large. Intermediate content of acetonitrile and water concluded with minimum retention factor. The mechanism was determined with use of pyridine in whole scale of acetonitrile concentration. In purely PALC conditions (low acetonitrile content) surface of silica exhibits strongly heterogenous character. High density hydrophobic siloxane groups take part in less than 10% of sample retention. Basically, pyridine retention is controlled by the active adsorption sites present on the surface of low-density silica. They can be attributed to hydrophobic micropores, which adsorb the pyridine molecules. In purely HILIC conditions (high acetonitrile content) active sites are occupied by ACN molecules, which are excess in the mobile phase. This prevents their hydrophobic interactions with pyridine. Therefore, single silanol groups (constituting 75%) and geminal and/or vicinal hydroxyl groups (constituting the remaining 25%) are responsible for the retention[137]. Efficiency measurements were carried out for the same Halo column, using caffeine and pure watereacetonitrile mobile phase, without ionogenic substance added. Retention factors for both mechanisms were determined in the range from 0.5 to 2.5 at room temperature. For such retention factors efficiency measurements were carried out. PALC mechanism is the most efficient at low retention factors k0 < 2, and should be avoided for strongly retained samples. For k0 > 2.5 height equivalent to a theoretical plate (HEPT) is lower for HILIC mechanism in compare to PALC [138].

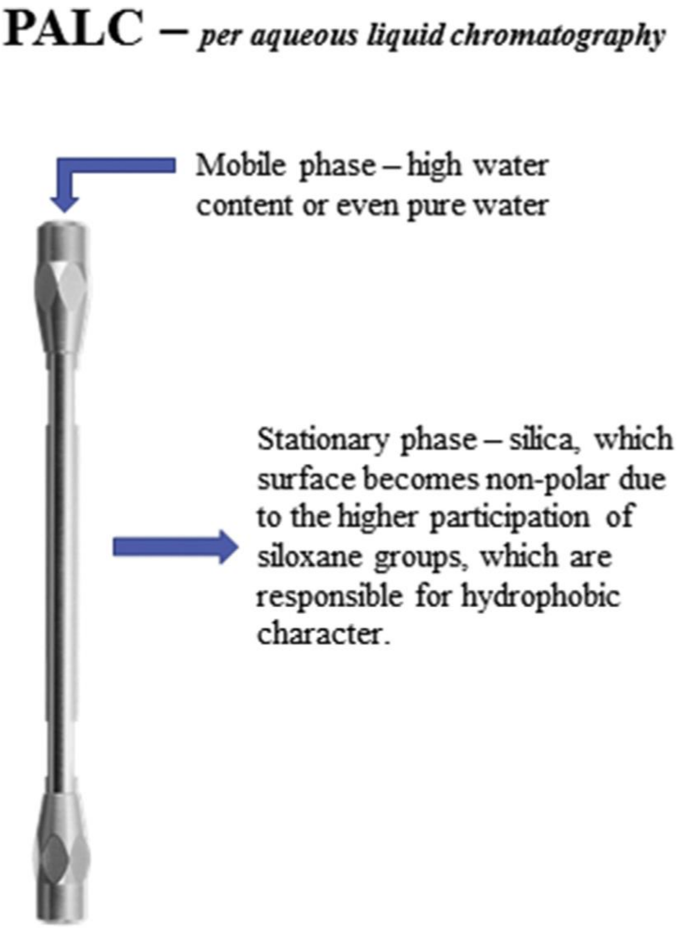

Fig. 4. Diagram showing the chromatographic arrangement used in the PALC technique [135].

The PALC technique was studied for various columns, polar analytes and ionic additives to the mobile phase. First, Li et al. used the polysaccharide-modified stationary phase (PMSP) column to determine six polar substances: melamine, vitamin B2, vitamin B6, caffeine, benzoic acid and hydroquinone [139]. Further studies confirm that the use of the PALC method has a comparable retention with HILIC for the determination of polar compounds. The connection of functionalized carbon nanoparticles (CNPs) obtained from corn stalk soot to the silica surface allows to obtain polar stationary phases working with both water-rich and acetonitrile-rich mobile phase [140]. The effect of the buffer or salt presence in the mobile phase (ammonium formate, pH = 5) on the separation of ionized catecholamines using a bare silica column (Zorbax-Rx-SIL) was then investigated. The poor peak shapes were obtained mainly due to overloading of few, but strong adsorption sites [141]. The use of 1.7-mm ethylene bridged hybrid silica stationary phase to determinate twelve imidazolium-based ionic liquid cations showed that PALC mode gives both hydrophobic and ion-exchange mechanism [142]. Fungicides containing polar groups are reluctant to partition into the water-rich layer at a high ACN content in the bulk phase. Therefore, the application of the PALC method allows to increase the retention at reduced ACN content in the mobile phase [143]. Attempts have also been made to use combined techniques. Matos et al. combined PALC with size exclusion chromatography (SEC) and diode array detector (PALCxSEC-DAD) to determine water-soluble organic matter (WSOM) in atmospheric aerosols collected at different seasons of the year from urban area [144]. PALC analyses are also used as a complement to RP-LC analyses, mainly due to their positive environmental and economic aspects. A silica-based column with attached Congo red molecules (Sil-CR) was used to determine four types of biogenic amines and five bases and nucleotides [145]. The results showed that PALC analysis in this case gives better separation than the use of acetonitrile-rich HILIC mode. Also, such a result gives useful information for exploration of the PALC chromatographic column materials. The most recent publications report on subsequent syntheses of materials for chromatographic columns packings, such as polysaccharide-modified stationary phase [146] and porous organic cage embedded C18 amide silica stationary phase [147] and separation and determination of groups of polar and hydrophilic compounds such as protein A [148], to develop the PALC mode.

The PALC method is a relatively new technique, covering the last decade. However, its development is observed mainly in the context of the analytical technique competing with HILIC, as well as due to its economic and ecological advantages. Research into the synthesis of new stationary phases used in PALC and separation of groups of polar and hydrophilic compounds will be the main issue of the development of this method

Water as a mobile phase at ambient temperature

The use of a fully aqueous mobile phase at room temperature is the most advantageous form when considering environmentally friendly liquid chromatography. Approximately ambient conditions are understood as analyses performed at temperatures below 60C. PALC is also considered as a type of these techniques (Fig. 4). A new subcategory name for such analyses has been proposed e wateronly reversed phase liquid chromatography (WRP-LC) [50]. Studies under such conditions were performed more than three decades ago [149]. Satisfactory results were achieved primarily due to the application of silica surface modification, e.g. by bonding hydrophobic alkyl chains (C-8). However, in later studies it was confirmed that the highly polar mobile phase favors a large proportion of surface groups of silanols, which influence the separation mechanism. The use of short alkyl chains (up to 4 carbon atoms) allows to obtain stable stationary phases due to their high surface coverage density. Connecting longer chains causes a decrease in coverage density, and at low content of organic solvent (less than 5–10%) there is a decrease in phase solvation and causes the phase tend to collapse [94,150].

In order to reduce the influence of free silanols on retention, polar-endcapped and polar-embedded stationary phases were used. Polar-endcapped stationary phases are obtained in two stages. In the first stage long chains, e.g. alkyl chains, are attached. In the second stage, unreacted silanols are endcapped by a specific reagent. Polar-embedded stationary phases are obtained by incorporating a polar functional group into the hydrophobic ligand of the stationary phase, which allows for better water solvation under highly aqueous conditions (Fig. 5). The advantage of these phases is that they can be used in RP-LC, different selectivity of polar compounds compared to standard alkyl stationary phases, the ability to work in highly aqueous conditions, even up to 100% water content and limited influence of surface bound silanols, which favors the lack of peaks tailing of basic compounds [94,151e162].

There were many works showing the possibility of separation of substances with a wide range of polarity, using pure water at ambient temperature as a mobile phase. Buszewski et al., in 1994 demonstrated the possibility of separating the group of alkylanilines using a chemically bound phase (CBP) in particular alkylamide (AA) phase [163]. The use of ODS-packed column modified with strongly positive/negative charges surfactant (ODS coated with zwitteragent) for separation of nucleosides and their bases as a representative of typical polar organic compounds, were proposed several times [164–166]. Separation of compounds with different hydrophobicity was carried out using Poly(N-isopropylcrylamide)- Modified Silica (PIPAAm-modified silica). The influence of temperature on resolution was investigated. It was shown that already at room temperature there is a possibility of effective separation of steroids [167]. Another polymeric stationary phase were used by Satínský et al. were analytes of different polarities were determinated [6]. Their main objective was to obtain a “green” method, so they used a column that would allow separation using a low-toxic mobile phase that is pure water. Kiridena et al. used their developed polar-endcapped chromatographic column (Synergi™ Hydro-RP) at room temperature and elevated temperature (not exceeding 65°C) [95]. The most recent studies confirm the use of polarembedded stationary phases for the separation of polar compounds in both HILIC and RP-LC. By selecting the appropriate polar groups, it is possible to obtain stationary phases that will be effective at room temperature, giving reasonable retention times. It is important that the stationary phase meets three basic requirements. The first one is the presence of polar and hydrophobic groups allowing to obtain specific properties of the phase surface. The second is to allow the adsorption of the analyte molecules, although it should be selective. The last requirement is to allow the water molecule

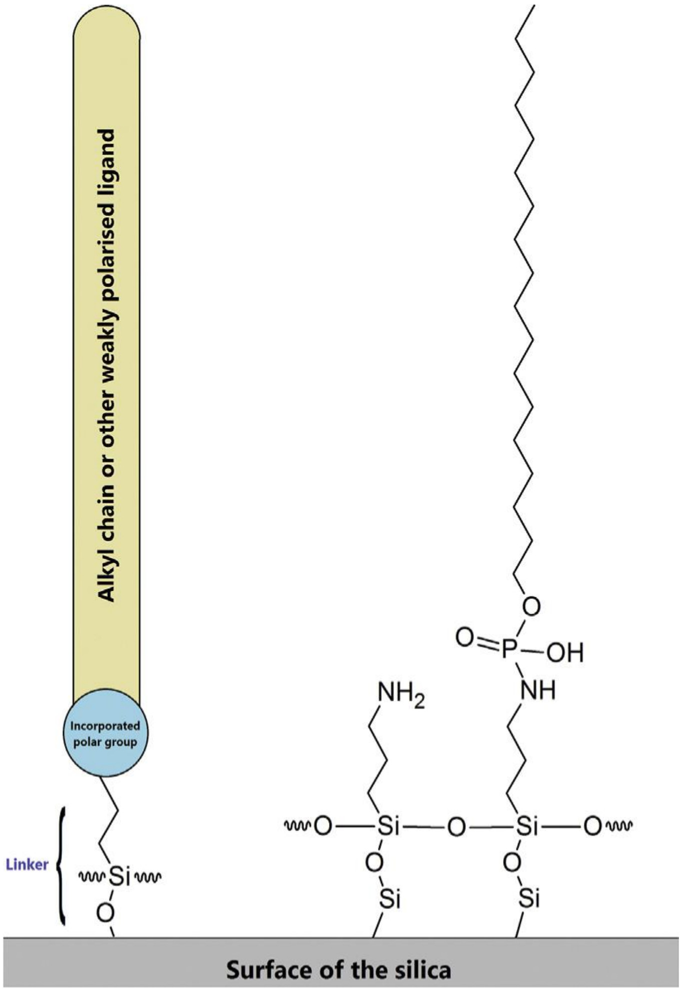

Fig. 5. Schematic structure of the polar-embedded stationary phase [155–162]. Linker is connected to the silica surface and to the incorporated polar group. A hydrophobic alkyl chain of different number of carbon atoms or another non-polar molecule (e.g. cholesterol) is connected to the polar group. The figure shows an example Amino-PC18 phase [159]

to elute the analytes at different times with retention factors between 1 and 10 and reasonable retention times [158,159]. Bocian and Krzeminska in their latest work published the results, which present the successful separation of the series of nucleic bases, nucleosides and purine alkaloids, using a completely aqueous mobile phase. They used a standard HPLC apparatus equipped with a diode-array UVeVis detector. The temperature of each measurement was 30°C. The N,O-dialkylphosphoramidate phase [152] and ester bonded phases [159] were used as a stationary phases. Because these are further studies demonstrating successful separation in pure water, such results confirm that the use of stationary phases from the polar-embedded group allows the separation of mixtures in a single component, aqueous mobile phase, at room temperature [158]. Exemplary results are presented in Fig. 6.

Most of the research using pure water as the only component of the mobile phase is directed towards the use of polar-embedded and polar-endcapped stationary phases. They work not only in RP and HILIC systems, but also with the use of pure water at room temperature as the only eluent. Research on the development of subsequent phases of this type will certainly allow for the best possible optimization of the separation in water-only liquid chromatography.

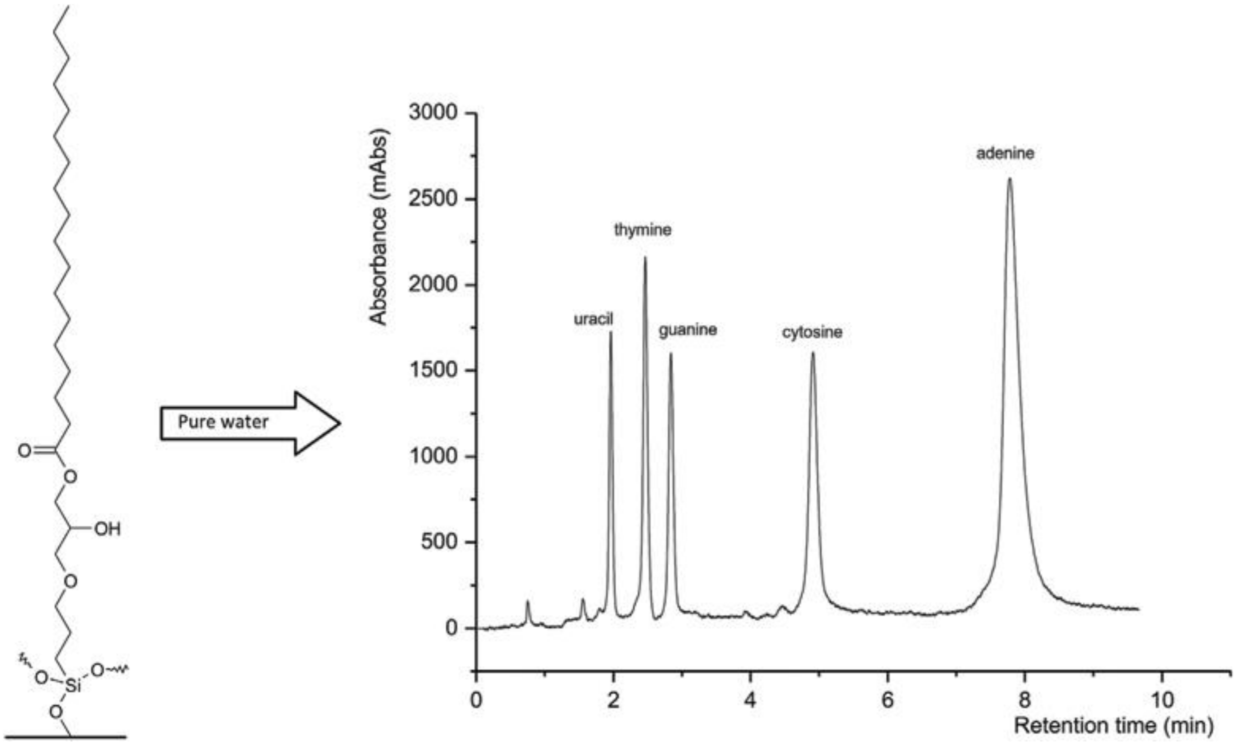

Fig. 6. Separation of five nucleosides on Ester-18 stationary phase using pure water as a mobile phase basis on [158].

Summary

The analytical methods presented in this review work prove that separation using high-performance liquid chromatography uses pure water as a mobile phase, it is achievable. There are different approaches, but all based on the selection of analysis conditions, stationary phase or possible additives to the mobile phase. The change in conditions is based on an increase in temperature, thanks to which water has different physical and chemical properties. There are changes in its polarity, dielectric constant, viscosity, surface tension and many other properties. The solubility of analytes, which at room temperature may be insoluble in such a strongly polar solvent, also changes. The stationary phase must have appropriate properties, in particular aqueous stability, thermal stability (using SHWC) and selectivity in relation to mixtures of compounds of different polarity. Thus, a number of stationary phases based on silica, carbon, polymers or metal oxides are obtained. Additions to the mobile phase in the form of acids or pHregulating compounds (buffers) enable more selective separation and often favor shorter analysis times. The main objective of this review work was to encourage the search for HPLC analytical methods that will allow for greater environmental friendliness.

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