

Chromatographic characterization of reversed-phase zirconia for the separation of phosphate esters of nuclear industry interest

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Introduction

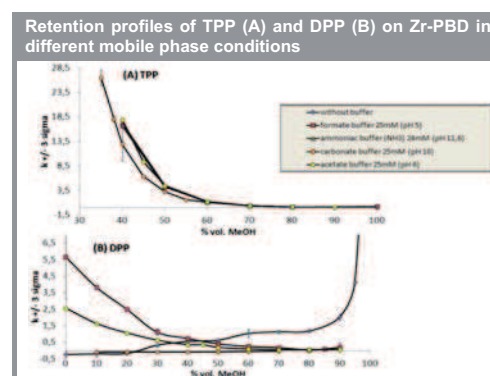
In the nuclear industry, tri-butyl-phosphate (TBP) is commonly used to extract plutonium and uranium during the reprocessing of radioactive nuclear wastes. During this process, TBP degrades to di-butyl-phosphate (DBP) and mono-butyl-phosphate (MBP) by dealkylation of one or two butoxy- groups, which consequently reduces the efficiency of the extraction procedure. It is therefore necessary to analyze the levels of TBP, DBP and MBP in waste fuel tanks as a routine quality control measurement of the nuclear reprocessing method. Today, ion-pairing liquid chromatography on C18 silica-based stationary phases (RPLC) is commonly used for such analytical issue. This technique allows the simultaneous separation of neutral and ionizable compounds through mixed-mode hydrophobic partition and ion exchange retention mechanisms. It suffers however of low repeatability of the surface chemistry of the dynamic ion-paired stationary phase, in addition to low pH and thermal stability of the silica-based supports in extreme conditions of pH and temperatures (i.e., for silica, the tolerated pH values are restricted between 2 and 8, and the temperature is below 80 °C). It is therefore important to find an alternative approach to the separation of these phosphorylated compounds. For instance, the use of hydrophobic supports based on metal oxides such as titania or zirconia seems to provide an original solution owing to the mixed-mode hydrophobic partition/ ion- and ligand exchange behavior of these phases. Moreover, these chromatographic supports can be operated in extreme conditions of mobile phase pH ($1 < \text{pH} < 14$), and temperature ($T > 150$ °C) unlike conventional silica-based materials. This article illustrates the studies we have performed on a hydrophobic zirconia stationary phase using tri-, di- and mono-phenyl- phosphates, as homologous molecules of butyl-phosphates, which can be easily monitored with a UV detector.

Experimental conditions

The chromatographic studies were performed on Thermo Surveyor HPLC system, equipped with a quaternary liquid pumping system, a manual injector (injection loop, 5 μ L) and a Photodiode Array detector (PDA). A Discovery Zr-PBD chromatographic column (50 x 4,6 mm, 3 μ m), consisting of poly-butadiene- physically coated on zirconia was investigated in RPLC mode. Mono-phenyl-phosphate (MPP), di-phenyl-phosphate (DPP) and tri-phenyl-phosphate (TPP) were used as test solutes. The UV detection was carried at 254 nm. The mobile phase consisted of a mixture of methanol and water and several salts with pH buffering capacity between 5 and 12 (e.g., sodium carbonate, ammonium acetate, ammonium formate, ammonia).

Results and discussion

Fig. A and B respectively illustrate the evolution of the retention factor (k') of TPP and DPP as a function of the organic content and the type of buffer used in the mobile phase. Fig.A shows that the retention factor of TPP decreases conversely to the percentage of methanol and does not depend on the pH or on the type of buffer. The retention profile of TPP follows therefore a typical hydrophobic partition mechanism in accordance with the neutral behavior of the test compound. In the case of DPP ($\text{pK}_a = 1,12$), a different behavior was observed because of the ionizable character of the solute.



The hydrophobic partition mechanism prevails under slightly acidic conditions in the presence of ammonium acetate and formate buffers in the mobile phase. In these conditions, the deviation noted between the retention profiles highlights the implication of the buffer anion specie in the interaction mechanism of DPP with the zirconia phase and attests the presence of mixed-mode retention. In basic conditions, ion-exclusion is consistent with an electrostatic repulsion mechanism. So, the different mechanisms of retention of DPP on Zr-PBD are more or less predominant depending on the pH of the mobile phase.

Conclusion

A good separation quality between the pThe mixed-mode retention mechanism found on Zr-PBD gives this phase great potentials for the separation of phosphate esters of nuclear industry interest.



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