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3	Article Copyright - Year	**Springer-Verlag Berlin Heidelberg 2014 (This will be the copyright line in the final PDF)**	
4	Journal Name	Analytical and Bioanalytical Chemistry	
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56	Schedule	Received	27 June 2014
57		Revised	29 August 2014
58		Accepted	16 September 2014
59	Abstract		
60	Keywords separated by ' - '	HPLC - Perfluoroalkyl acids - Endocrine disruptors - Trace elements - Surfactants - Fluorous	

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61 Foot note information

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Anal Bioanal Chem
DOI 10.1007/s00216-014-8198-5

TRENDS

New insights into perfluorinated adsorbents for analytical and bioanalytical applications

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Received: 27 June 2014 / Revised: 29 August 2014 / Accepted: 16 September 2014
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Abstract Perfluorinated (*F*-) adsorbents are generally prepared by bonding perfluoro-functionalized silanes to silica gels. They have been employed for a long time essentially as media for solid-phase extraction of *F*-molecules or *F*-tagged molecules in organic chemistry and heterogeneous catalysis. More recently, this approach has been extended to proteomics and metabolomics. Owing to their unique physicochemical properties, namely fluorophilicity and proteinophilicity, and a better understanding of some fundamental aspects of their behavior, new applications of *F*-adsorbents in the field of environmental science and bio-affinity studies can be envisaged. In this article, we revisit the most important features of *F*-adsorbents by focusing, in particular, on some basic information that has been recently obtained through (nonlinear) chromatographic studies. Finally, we try to envisage new applications and possibilities that *F*-adsorbents will allow in the near future.

Keywords HPLC · Perfluoroalkyl acids · Endocrine disruptors · Trace elements · Surfactants · Fluorous

Introduction

Highly fluorinated compounds (*F*-compounds) are characterized by the presence in their structure of a portion in which a substantial number of hydrogen atoms (typically 7 to 20) attached to carbon atoms are replaced with fluorine atoms. This gives the molecules specific properties that are different from those of their parent hydrocarbon analogs. In the terminology of fluorous chemistry a portion or domain of a molecule rich in sp^3 carbon–fluorine bonds is termed a fluorous label or tag (more specifically, if at least six fully fluorinated sp^3 carbons are present, the *F*-portion is referred to as a "ponytail") [1].

F-alkyl chains are bulkier and more rigid than alkyl chains (cross section of around 30 $Å^2$ vs. about 20 $Å^2$ for alkyl chains) and adopt a helical-like structure in place of the typical planar zigzag structure of alkyl chains. The stiffness of *F*-alkyl chains is claimed to be responsible, on the one hand, for their ordered stacking and, on the other, for their slower equilibration and exchange kinetics compared with those of alkyl chains [2–5].

F-alkyl chains are more hydrophobic than alkyl chains of similar length. According to the Hildebrand and Scott solubility scale, for instance, the solubility parameter (that strongly correlates with polarity) for *F*-alkanes is roughly 5 $cal^{1/2}$ $cm^{3/2}$, whereas it is 7 for *n*-alkanes (and 15 for water) [6]. In addition, *F*-alkyl chains posses a lipophobic character (sometimes referred to as oleophobicity [1]) and are less polarizable than the corresponding hydrocarbons, as indicated by their Kamlet–Taft dipolarity/polarizability parameters and by lower refractive indexes than hydrocarbons [7]. These characteristics, together with the strength of the C–F bond and the enhanced electroattracting character of fluorine (that reinforces the C–C backbone), explains the well-known chemical inertness and thermal stability of perfluorocarbons [1].

Perfluorocarbons have recently found important applications in many fields of research, including synthesis, catalyst technology, adsorption/purification processes, materials chemistry, and biomedical applications. Table 1 lists some of the most popular perfluorinated materials for applications in HPLC and fluorous solid-phase extraction (F-SPE).

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t1.1 **Table 1** Commercially available perfluorinated stationary phases for both HPLC and F-SPE applications

t1.2 Brand name	Provider	Bonding phase	Particle size (μm)	Pore size (Å)	End-capped
t1.3 Fluoro*Flash*	Fluorous Technologies Inc.	C_8F_{17}	5; 40	60	No
t1.4 FluoroSep-RP Octyl	ES	C_8F_{17}	5	60	N/A
t1.5 Fluofix	Wako	C_6F_{13}-branched	5	120; 300	No, yes
t1.6	Thermo	C_6F_{13}-branched	5	100; 300	Yes
t1.7 Fluophase RP/WP	Thermo	C_6F_{13}	5	100; 300	Yes
t1.8 Tridecafluoro	Silicycle	C_6F_{13}	40; 63	60	Yes
t1.9 FluoroSep-RP Propyl	ES	C_3F_7	5	300	N/A
t1.10 Fluorochrom	Silicycle	N/A	40; 63	60	No

N/A not available

Perfluorinated (*F*-) adsorbents

F-silica gels and fluorophilicity

F-silica gels have the general structure silica–O–$Si(Me)_2(CH_2)_n$ R_f, where n is either 2 or 3 and R_f is C_6F_{13} or C_8F_{17} [1]. Sometimes, pentafluorophenyl (PFP)-functionalized silica gels have been considered *F*-materials but, strictly speaking, they are not and will not be considered in this review.

Since their first appearance in the early 1980s, *F*-silica gels, thanks to their extreme hydrophobicity and low polarity, were claimed to be ideal candidates as adsorbents for the reversed-phase (RP) separation of large biomolecules under nondenaturating conditions (i.e., with minimum amount of organic modifier in the mobile phase) [8, 9]; however, the field has not been explored in depth and *F*-adsorbents have never actually been considered a real alternative to traditional RP phases, such as octyl- (C_8) or octadecyl-functionalized (C_{18}) silica gels. In contrast, *F*-silica gels have been applied as adsorbents for F-SPE and separation of fluorous molecules from non-fluorous ones and from each other [10, 11]. The unique ability of *F*-molecules to recognize other molecules possessing an *F*-portion is referred to as fluorous affinity or fluorophilicity. It arises from selective, strong noncovalent interactions between the perfluoroalkyl segments of molecules, in a sort of "like dissolves like" interaction.

On the basis of the concept of fluorophilicity, a series of cutting edge applications of *F*-adsorbents have appeared in recent years in the omics sciences [12, 13], food chemistry [14], environmental science [15], amongst others.

Perfluoro-selectivity through liquid chromatography studies

Fluorophilicity is generally quantified by fluorous/organic liquid/liquid partition coefficients [1]. High-performance liquid chromatography (HPLC) offers an alternative approach to evaluate fluorous phase affinity, when a perfluoroalkyl stationary phase is used.

Indeed, the dependence of the logarithm of the chromatographic retention factor (k) upon the number of perfluorocarbon units (n_{CF_2}) in the backbone chain of a perfluoroalkyl homologous series (at fixed mobile phase composition) permits the estimation of the change of Gibbs free energy, ΔG_{CF_2}, for the transfer from the mobile to the stationary phase of a perfluoromethylene group as follows [15–18]:

$$\Delta G_{CF_2} = -RT\frac{d\ln k}{dn_{CF_2}} = -RT\ln \alpha_{CF_2} \quad (1)$$

where α_{CF_2}, R and T, are the selectivity, the universal gas constant, and the absolute temperature, respectively. As an example of this approach, Fig. 1 shows how ln k changes by changing the amount of acetonitrile in the mobile phase for four perfluoroalkyl acids of environmental concern. In the region delineated by green points, ln k decreases quasi-linearly with increasing organic modifier. At each mobile phase composition, the slope of the ln k vs. n_{CF_2} plot gives the natural logarithm of the selectivity (for the sake of clarity, the case of 50 % acetonitrile in the mobile phase is illustrated in Fig. 1). Table 2 reports ΔG_{CF_2} values (calculated by this approach through Eq. 1) as a function of the mobile phase composition for two different stationary phases, a traditional octadecyl and a straight-chain perfluorinated one [17]. Even if the transfer of the CF_2 moiety from the mobile to the stationary phase is thermodynamically favorable on both phases at all mobile phase compositions (its value always being negative), the ability of the *F*-adsorbent to "recognize", and thus to stabilize, this moiety is markedly larger than that of the C_{18} phase. This is demonstrated by absolute values of ΔG_{CF_2}, on average much larger (+70 %) on the *F*-adsorbent than on the C_{18} one.

Another example of the improved selectivity of fluorinated stationary phases over hydrocarbon ones towards the separation of fluorinated solutes is given in Fig. 2, where chromatograms of the separation of benzene and five fluorinated analogues on the two phases are compared [19].

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Adsorption of organic compounds from multicomponent mixtures on *F*-adsorbents

The adsorption of organic compounds from multicomponent mixtures on *F*-adsorbents can be measured by several techniques, including HPLC [20, 21]. When the adsorption isotherm is measured through chromatography, the information can be given either as the excess or absolute isotherm. The quantity directly measured in an adsorption experiment is the excess (usually indicated by Γ). It is defined as the excess of solute contained in the adsorption system (considered as a whole) compared to what would be present in a hypothetical system where solute concentration is uniform throughout the whole volume of the eluent and equal to the equilibrium concentration in the bulk phase of the real system [22–24]. On the other hand, the total adsorbed amount (q) is the amount of solute contained in an adsorbed layer of finite thickness. Clearly the definition of the adsorbed layer is arbitrary and needs the adoption of some convention [25, 26]. Figure 3 shows both types of isotherms measured for the adsorption of acetonitrile from water/acetonitrile binary mixtures on a straight-chain perfluorohexylethylsiloxane-bonded stationary phase [27]. Acetonitrile is strongly adsorbed by the *F*-phase with a saturation value of roughly 13 μmol of acetonitrile adsorbed per square meter of solid. The negative excess of acetonitrile at organic-rich mobile phase compositions corresponds to a positive excess of water on the surface. This is due to the adsorption by unreacted silanols, which remain on the silica surface after its functionalization, that, under these conditions, have not been saturated yet [27].

Adsorption isotherm data allow one to estimate several characteristic properties of the system under examination, including solvent fluorophilicity, interfacial tension at the solid/liquid interface, and wetting properties, which all have important implications for technological applications of catalysis, material engineering, environmental science, the fluorotelomer industry, pollution research, etc. as will be further discussed in the "Outlook" section.

Retention mechanisms in liquid chromatography with *F*-stationary phases

A recent study focusing on the chromatographic behavior of silica-based *F*-adsorbents revealed that, under typical RP conditions (with aqueous acetonitrile eluents), the major features described for these phases can be understood and rationalized in terms of traditional liquid–solid chromatographic models based (1) on the formation of a mixed stationary phase and (2) partitioning of solutes between the mobile and this stationary phase [17]. As an example, the so-called U-shape retention behavior of *F*-adsorbents (i.e., the U-shaped dependence of ln k with increasing amount of acetonitrile in the mobile phase, see Fig. 1), which in some cases has been described as a sort of peculiar characteristic of these materials [28], can be explained by considering a mixed-mode retention mechanism in which both fluorophilic (hydrophobic) and silanophilic (hydrophilic) interactions are simultaneously present (exactly as happens with C_{18} silica-based adsorbents) [17].

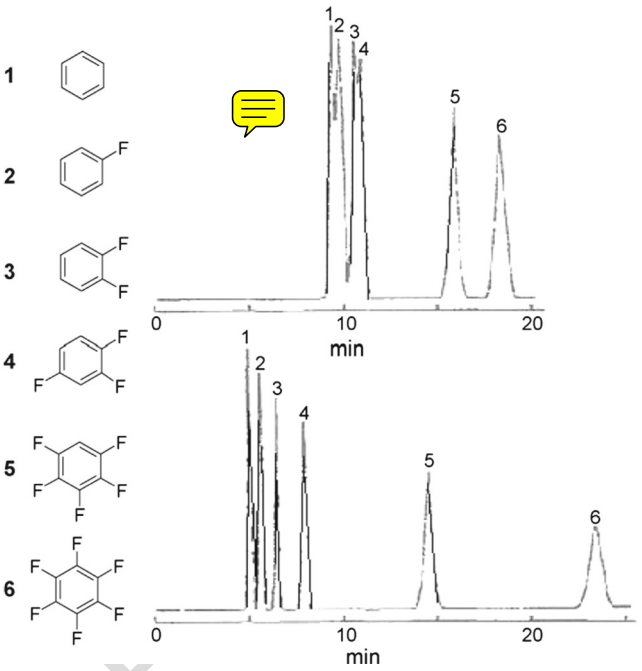

Fig. 1 3D plot showing the dependence of ln k and both the mobile phase composition (expressed as volume fraction of acetonitrile) and number of perfluorocarbon units in the backbone chain, n_{CF_2} . Sample, mixture of four perfluoroalkyl acids (perfluoropentanoic, $n_{CF_2} = 4$, perfluorohexanoic, $n_{CF_2} = 5$, perfluoroheptanoic, $n_{CF_2} = 6$, perfluorooctanoic $n_{CF_2} = 7$). Column, perfluorohexylpropylsiloxane-bonded silica (Fluophase-RP from Thermo Scientific); mobile phase, water/acetonitrile mixtures (+0.1% v/v formic acid); temperature, 298 K. Adapted from ref. [15]

Although *F*-adsorbents certainly exhibit a different selectivity than traditional RP adsorbents (e.g., C_{18} or C_8), the true peculiarity of *F*-adsorbents is when they are used with *F*-compounds. Fluorophilicity can be thus modulated by careful choice of the eluent composition [15, 17]. With aqueous/acetonitrile mixtures, fluorophilicity can be maximized by maximizing the content of water in the mobile phase (to reduce the competitive adsorption of acetonitrile). It has been demonstrated, however, that to allow the complete wetting [29] of the (meso)porous structure of silica-based *F*-adsorbents, a minimum amount of organic (approx. 5–10 % in volume) is necessary in the eluent [30].

Outlook

In this section, we briefly present our views on the future of *F*-adsorbents by trying to anticipate new solutions and

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t2.1 **Table 2** Free-energy change, ΔG_{CF_2}, for the transfer from the mobile to the stationary phase of a CF_2 unit as a function of mobile phase (MP) composition (expressed as acetonitrile volume fraction) on an *F*- and an octadecyl stationary phase

	MP	*F*-alkyl (J/mol)	C_{18} (J/mol)
t2.2			
t2.3	0.5	−2,239	−1,399
t2.4	0.6	−2,008	−1,209
t2.5	0.7	−1,777	−1,053
t2.6	0.8	−1,679	−902
t2.7	0.9	−1,427	−761

Adapted from ref. [17]

F-alkyl, perfluorohexylpropylsiloxane-bonded silica, Fluophase-RP from Thermo Scientific; C_{18}, octadecylethyl-bridged hybrid organic/inorganic, BEH-C_{18} from Waters; temperature, 298 K

opportunities that, in our opinion, will be offered by these materials in several different fields of research.

The most important area in which we believe *F*-adsorbents will contribute to the advancement of knowledge and technical know-how is environmental chemistry. In particular, we are thinking about the numerous classes of perfluoroalkyl and polyfluoroalkyl substances and their several homologues and isomers. Concern about the effects of *F*-compounds on the environment and human health has dramatically increased in recent years as these compounds are toxic, extremely resistant to degradation, bioaccumulate in food chains, and can have long half-lives in humans [31]. In spite of the complexity and variety of these compounds, the interest of the scientific community has focused almost exclusively on perfluoroalkylcarboxylic and perfluoroalkylsulfonic acids. Even though numerous studies have been published in the literature and much information has been gathered about the sources, fate, transport, and toxicity of these species, some fundamental aspects of their physicochemical properties and

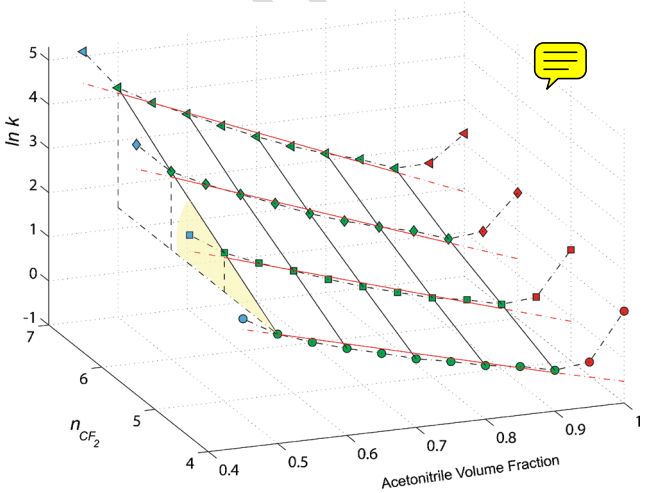

Fig. 2 Chromatographic separation of a mixture of benzene and five different fluorinated analogues on a C_{18} (*top*) and a C_8F_{17} (*bottom*) column. Taken with permission from ref. [19]

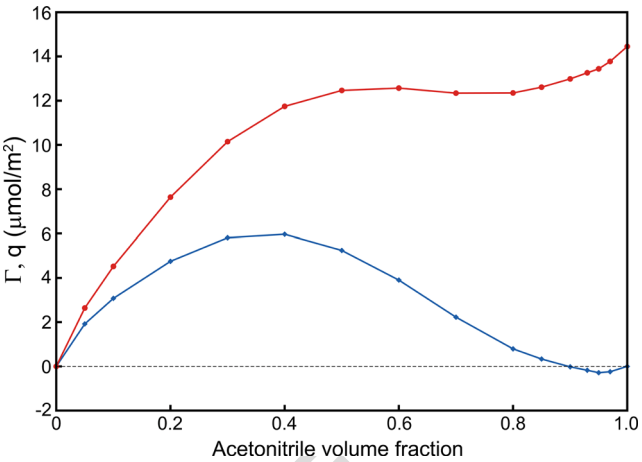

Fig. 3 Excess (*Γ*, *blue line*) and absolute (q, *red line*) adsorption isotherm of acetonitrile from water/acetonitrile binary mixtures on a straight-chain perfluorohexylethylsiloxane-bonded stationary phase. Temperature, 298 K. Adapted from ref. [27]

partitioning behavior are poorly understood and widely debated. As an example, the pK_a value of perfluorooctanoic acid is reported to vary from 0 (i.e., a strong acid) to about 4 (relatively weak acid) [32–34]. Since transport properties in the environment are strictly dependent on the chemical form of molecule (in this case ionic or neutral), and thus on pH, one understands how fundamental research in the field is still needed.

There are also many other *F*-compounds, whose presence in the environment has been recently demonstrated (e.g., perfluoroalkane sulfinic acids and perfluoroalkyl phosphinic and phosphonic acids [35]), for which the scenario is even worse because practically no studies have been performed on them.

Still another example is the class of fluorotelomers and fluorotelomer-based products recently brought into the spotlight [36]. This class includes, among others, many antistaining and antiwetting agents, which are widely employed in everyday life. Nevertheless, systematic studies about their stability and degree of exposure in both humans and the environment not only to them but also to their degradation products are substantially missing.

As is illustrated by these examples, many questions about *F*-compounds are unanswered and others will arise as more is learned about these ubiquitous anthropogenic substances [31]. In the near future, it is reasonable to anticipate that there will be an increasing demand by both the scientific community and control and regulatory agencies for efficient, selective, and easy-to-automate analytical methods and tools for the determination, monitoring, and removal of *F*-compounds in matrixes of different origin (including biological samples). In all these cases, the potential of *F*-adsorbents is evident. Owing to their intrinsic affinity towards *F*-compounds, *F*-adsorbents look like being the perfect counterpart for the separation and capture of these species [15, 29, 30].

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Apart from the already demonstrated use in proteomics [12] and metabolomics [13] for the separation of fluorous-tagged molecules, another field where we consider the use of *F*-adsorbents to be potentially very useful is as stationary phases for bioaffinity chromatographic studies. This consideration comes from the evidence that *F*-compounds preferentially bioaccumulate in body compartments high in protein content (this property of *F*-compounds is known as proteinophilicity), such as the liver, kidney, and blood. For instance, it has been demonstrated that human serum albumin (HSA), the most abundant protein in blood plasma, binds through specific high affinity interactions with several *F*-compounds [37–39]. Thus, one might imagine using these adsorbents either directly as supports for binding studies of proteins by means of nonlinear chromatographic techniques [40] or as a sort of pre-fractionation system (possibly in-line) for proteome analysis of low-abundance proteins [41]. Indeed these proteins, whose diagnostic potential is very relevant, are often extremely difficult to detect because of the masking presence of high-abundance serum proteins.

Finally, another field of application where *F*-adsorbents can be useful is heterogeneous catalysis for investigating and designing new recovery strategies of fluorous catalysts and reagents without using fluorous solvents. This is strictly connected to the possibility of studying the affinity of different solvents, including supercritical CO_2, or multicomponent solvent mixtures towards *F*-materials through dynamic (chromatographic) adsorption studies.

Acknowledgments The authors thank the Italian University and Scientific Research Ministry (PRIN 2012ATMNJ_003). NM thanks Laboratory Terra&Acqua Tech, member of the Energy and Environment Cluster, Technopole of Ferrara of Emilia-Romagna High Technology Network.

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