



A survey of analytical methods employed for monitoring of Advanced Oxidation/Reduction Processes for decomposition of selected perfluorinated environmental pollutants[☆]



Marek Trojanowicz^{a,b,*}, Krzysztof Bobrowski^{a,c}, Bogdan Szostek^d, Anna Bojanowska-Czajka^a, Tomasz Szreder^a, Iwona Bartoszewicz^a, Krzysztof Kulisa^a

^a Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

^b Department of Chemistry, University of Warsaw, Pasteura 1, 02-095 Warsaw, Poland

^c Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

^d DuPont Corporate Center for Analytical Sciences, Wilmington, DE 19807, USA

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ABSTRACT

The monitoring of Advanced Oxidation/Reduction Processes (AO/RPs) for the evaluation of the yield and mechanisms of decomposition of perfluorinated compounds (PFCs) is often a more difficult task than their determination in the environmental, biological or food samples with complex matrices. This is mostly due to the formation of hundreds, or even thousands, of both intermediate and final products. The considered AO/RPs, involving free radical reactions, include photolytic and photocatalytic processes, Fenton reactions, sonolysis, ozonation, application of ionizing radiation and several wet oxidation processes. The main attention is paid to the most commonly occurring PFCs in the environment, namely PFOA and PFOS. The most powerful and widely exploited method for this purpose is without a doubt LC/MS/MS, which allows the identification and trace quantitation of all species with detectability and resolution power depending on the particular instrumental configurations. The GC/MS is often employed for the monitoring of volatile fluorocarbons, confirming the formation of radicals in the processes of C–C and C–S bonds cleavage. For the direct monitoring of radicals participating in the reactions of PFCs decomposition, the molecular spectrophotometry is employed, especially electron paramagnetic resonance (EPR). The UV/Vis spectrophotometry as a detection method is of special importance in the evaluation of kinetics of radical reactions with the use of pulse radiolysis methods. The most commonly employed for the determination of the yield of mineralization of PFCs is ion-chromatography, but there is also potentiometry with ion-selective electrode and the measurements of general parameters such as Total Organic Carbon and Total Organic Fluoride. The presented review is based on about 100 original papers published in both analytical and environmental journals.

1. Introduction

Perfluorinated organic compounds (PFCs) or perfluoroalkyl substances (PFASs) are particular types of anthropogenic environmental pollutants. Although technologies of their production or technologies related to their applications have been both known and utilized since 1940s, for long decades their role as synthetic pollutants emitted to the natural environment by various pathways was not very much considered by environmental chemists, toxicologists, or food chemists. The first observations of organic compounds containing fluorine in human organisms at the end of 1960s did not change this fact too [1]. It can be

assumed that this was caused by their recognized chemical inertness and trace (or even ultra-trace) contamination in aquatic biota. Only in the beginning of 2000s works by Moody and Field [2] or Giesy and Kannan [3], considering environmental implications of the use of fire-fighting foams with PFCs or global distribution of perfluorooctanoate in wildlife, respectively, resulted in avalanche increase of an interest in those anthropogenic pollutants.

The main feature of the PFCs structure is a long 4–14 carbon atoms alkyl chain, in which all hydrogen atoms are replaced by fluorine ones. This results in a strong surface activity of these molecules. Due to the presence of the C–F bond, known as the strongest covalent chemical

[☆] Dedicated to Professor Gary D. Christian on his 80th birthday anniversary.

* Correspondence to: Institute of Nuclear Chemistry and Technology, Laboratory of Nuclear Analytical Methods, ul. Dorodna 16, 03-195 Warsaw, Poland.
E-mail address: trojan@chem.uw.edu.pl (M. Trojanowicz).

bond, most of PFCs are exceptionally stable in the environment. Besides the hydrophobic fluoroalkyl group, PFCs contain terminated hydrophilic groups such as e.g. carboxylic, sulfonic, sulfonamide or phosphonic. The surface-active properties and extraordinary chemical and thermal inertness brought about a variety of applications, of which most important ones are the protection of carpets, impregnation of textiles and leather, coating paper and board as well as fire-fighting foams [4]. They are also widely used as surfactants in cosmetics, in electronics, in etching; they also serve as polymerizations aids. This wide scope of applications, together with their chemical inertness has resulted in their global presence in the environment. Two most commonly detected PFCs, both in the natural environment and in living organisms, include perfluorooctyl sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) [3–6].



Perfluorooctanoic acid (PFOA) Perfluorooctanesulfonic acid (PFOS)

PFOS is the predominant PFC detected in the environment [7,8]. It comes from manufacturer releases when employed in specialized industrial processes; it is also a component of fire-fighting foams and the impregnating agent. In 2009 it was added to the list of persistent organic pollutants (POPs) of the Stockholm Convention, next to numerous pesticides and several groups of polychlorinated and polybrominated industrial pollutants [9]. The Stockholm Convention is the United Nations Treaty signed in 2001 and it aims to eliminate or limit the production of POPs. Between 2000 and 2002 PFOS was phased out of the production in USA by its main producer The 3 M Company [10].

Perfluorinated carboxylic acids (PFCAs), including PFOA, were emitted to the environment both from their manufacture and use [11]. The main indirect source of emission is the degradation of semivolatile fluorotelomer alcohols, which are raw materials used in the manufacture of surfactants and fluoropolymers [12]. The studies on photochemical reactivity of PFOA under conditions representing surface water led to the conclusion that the photochemical half-life for PFOA can be estimated to be at least 256 years when close to the surface and more than 5000 years when in the mixing layer of the open ocean [13]. As a result of the US EPA activity in this field, eight major companies producing and using PFOA agreed that they would phase out PFOA from both production and use by the end of 2015 [9]. The main trend in this field is the replacement of PFOS and PFOA by less bioaccumulative perfluorinated surfactants with shorter fluoroalkyl chains. It has to be pointed out that since 2002 a geographical shift of industrial sources of PFCAs from North America, West Europe and Japan to emerging Asian economies, especially China, has been indicated [14].

The occurrence of PFOA and PFOS in natural waters, waste waters, or drinking waters in different geographical localization is already very well documented in vast scientific literature, including also numerous review papers, see e.g. [5,6,15,16]. For instance, data from 10 countries on surface waters show PFOA contamination from 0.01 to almost 10^5 ng/L, with a median concentration 3.1 ng/L, while for PFOS from about 10^{-3} to 10^4 ng/L with a median concentration 3.2 ng/L [16]. The level of PFOS in open ocean water is reported in the range 1.1–73 pg/L, whereas for PFOA from 15 to 439 pg/L [5]. Lower PFOS values are explained by the lower bioaccumulation potential of PFOA. The reported contents of both considered PFCs in drinking waters in different countries are also in a very wide concentration ranges. For PFOA, including extreme values, this range is from 0.01 up to even 10^4 ng/L, while for PFOS from 0.1 to 100 ng/L [15]. Typical concentrations in drinking waters in different countries are < 100 ng/L PFOA and < 50 ng/L PFOS, except for the point source contaminations. Reported values of percent removal in different routine treatment

processes depend strongly on the influent sources and employed processes, and can vary from few percent up to complete removal [15].

A wide distribution of PFCs in the natural environment has obvious impact on their presence in living organisms, especially that the half-life of considered PFCs in water at 25 °C is estimated as > 92 years for PFOA, and > 41 years for potassium salt of PFOS [17]. The PFOA content in human blood serum in industrialized countries exhibits a relatively narrow range between 2 and 8 µg/L [18], although the mean values may reach 41.6, and even 354 µg/L [19]. The main source is the food intake, while drinking water exposure is a predominant for population near sources of contaminated drinking water. Mean PFOS values in North America human population are within the range 10–73 µg/L, while in adult population worldwide from < 1 up to

130 µg/L [19]. Those values certainly are of special importance for a wide toxicological studies on health hazards of those compounds, related e.g. to developmental toxicity, immunotoxicity or hepatotoxicity. In the study of human exposure to PFCs it was shown that the content of both PFOA and PFOS in human serum is closely connected with historical production of perfluorooctanesulfonyl fluoride (POSF), which is used to make PFOS [18]. The studies carried out e.g. in Norway proved that food (seafood in particular) can be considered as a major source of PFCs in human organisms [20]. However, a commonly reported presence of those compounds in drinking water (see e.g. [21]) also contributes to it to a certain extent, in spite of their relatively low detected concentrations. The serum/plasma elimination half-lives were reported as 5.4 and 3.8 years for PFOS and PFOA, respectively [19].

A common presence of anthropogenic PFCs in human organisms on a global scale is, on the one hand, a reason for conducting wide-scope toxicological studies, (see example reviews [22,23]), and, on the other hand, it is also a reason for conducting intense studies on the development of efficient methods of their removal from the environment [24]. Although in numerous original works one can find conclusions about probable links between the exposure to PFOA and high cholesterol, ulcerative colitis, thyroid disease, testicular cancer, kidney cancer, and pregnancy-induced hypertension [25], the epidemiologic evidence still remains limited and the collected data has so far been insufficient to draw firm conclusions [22].

Wide interest in the environmental role and interactions of PFCs with living organisms requires to apply especially sensitive and selective analytical methods for their determination. It seems to be not without reason that the evident beginning of those multidirectional studies in early 2000s coincided with a rapid progress of liquid chromatography methods coupled with mass spectrometry (LC/MS). A solid position which these most powerful methods have achieved in the field of qualitative and quantitative analysis of organic compounds in the environment, together with the appearance of commercial LC/MS instruments on the market, was also a key factor here [26]. As it was convincingly proved by certain reviews of analytical methods for the determination of PFCs published over the last decade [27–30], these methods are fiercely predominated in the analysis of environmental samples, foods and biological materials. Because of the trace level of those analytes and complex matrices, the LC/MS analyses are usually combined with the sample clean-up and preconcentration steps, mostly with the use of solid-phase extraction methods [31]. Due to a vast variety of PFCs occurring at trace level in environmental samples, a very practical solution for preliminary screening of the presence of

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