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Perfluorinated Surfactants in Environment – Their Sources, Analytical Methods of Determination, and Removal

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Abstract - The important group of anthropogenic pollutants from the point of view of environmental protection are perfluorinated anionic surfactants, in which in long alkyl chains all hydrogen atoms are replaced by fluorine atoms. These compounds are widely used on industrial scale in fire-extinguishers and for impregnation of numerous materials, in cosmetics and household products. Their environmental threat results first of all from a very large chemical stability in environment, comparable to common persistent organic pollutants such as chloroorganic pesticides, polycyclic aromatic hydrocarbons or polychlorinated biphenyls. Since beginning of 1990-ties it is known that they occur practically all over the globe, as they were detected in surface waters in the most remote regions on the Earth and in organisms of wild animals in all continents, in tissues of fishes and birds. They are commonly detected in human organisms, being a serious health threat because *e.g.* of destruction of lipid balance and possibility of their incorporation into a bilayer lipid cell membranes. The most commonly detected compounds in environment are perfluorinated octanoic acid (PFOA) and perfluorinated octanesulfonic acid (PFOS).

The environmental proliferation of perfluorinated compounds (PFC) in a global scale, their presence in organisms of animals and humans even in a very remote locations, and including them into Persistent Organic Pollutants, are the main reasons stimulating an intensive development of analytical methods for their determination. Determination of PFCs in different matrices is a very tough challenge for analytical chemists. In spite of a great progress in development of new methods and application of increasingly sophisticated instrumentation, still numerous problems and challenges remain to solve. Most commonly employed methods are predominated by chromatographic ones, mostly with mass spectrometry detection, but HPLC can be also employed with conductivity or fluorimetric detection, while GC with flame ionization or electron capture detections. An increasing attention is focused in recent years on determination of branched isomers of perfluoroalkyl compounds. Another difficulty is a limited number of available standards, and especially of the certified reference materials. From one side it is necessary to develop new methods and improve instruments *e.g.* for separation of isomers of PFCs, but on the other hand there is need for much simpler methods and instruments, enabling wide routine monitoring of those pollutants in environment. Their large variety in analyzed samples, makes those determinations very difficult and time consuming, hence it seems that for common monitoring a very helpful alternative can be evaluation of such total indices as Extractable Organic Fluorine, or Total Organic Fluorine. The trend observed in last years is also increasing interest in determination of PFCs in foods for tracking the pathways of human exposure.

The common occurrence of perfluorinated surfactants in environment is a reason of increasing interest in development of methods of their removal from waters and wastes. The classical methods of their removal from waters include reverse osmosis, sorption on activated carbon, but also sonochemical pyrolysis or incineration. The decomposition of perfluorinated compounds with release of total fluorine can be carried out with various combustion methods or by the use of a very strong reducing agents such as *e.g.* metallic magnesium in supercritical carbon dioxide, sodium in dry ammonia or sodium biphenyl. These methods, because of high cost of instrumentation and reagents, are employed mostly in micro-scale, for instance for analytical purposes. For technological purposes, including environmental protection, the studies on biodegradation and use of advanced oxidation processes with application of radical reactions are carried on. Recently also reductive defluorination

e.g. of perfluorooctane sulfonate (PFOS) with Ti(III)-citrate and vitamin B_{12} as catalyst was reported. The obtained results suggest the microbial transformation of some PFOS isomers might be possible in anaerobic environments. To increasingly investigated methods of removal of organic compounds which are anthropogenic environmental pollutants belong methods of advanced oxidation processes (AOP), based on the use of radical reactions. One of these processes is application of ionizing radiation, which in case of irradiation of aqueous solutions is an efficient source of radicals both of oxidizing and reducing properties, which can react with organic pollutants. There is already broad literature on application of AOPs with ionizing radiation for decomposition of numerous groups of organic pollutants in waters and wastes, including also surfactants, both of industrial and municipal origin. In this work aqueous solutions of PFOA and PFOS were irradiated with γ irradiation and electron beam in different chemical conditions and with different radiation dose. For the examination of effectiveness of decomposition of perfluorinated surfactants capillary electrophoresis and HPLC with different detections were employed.