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SURVEY ON PERFLUORINATED COMPOUNDS AND THEIR FORMATION POTENTIALS IN COSMETICS IN ASIAN AND EUROPEAN COUNTRIES

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1. Introduction

Perfluorinated compounds (PFCs) are a group of anthropogenic organic florinated compounds which have been widely used in many products. PFCs have been detected from water environment and wild animals[1]. Recently, it has been a growing concern about influences to fetal health from PFCs exposure since it has been detected from blood and breast milk of pregnant women[2]. Therefore, fluoropolymer manufactures have committed completely no using perfluorooctanoic acid (PFOA) by 2015 under a stewardship program of U.S.EPA[3]. In addition, they decided to restrict manufacture products using long chain PFCs from 2016[4]. Main pathways of human exposure to PFCs have been discussed as food items, household dust and drinking water[5]. Cosmetics have been paid attention as one of PFCs exposure pathways. Nicolopoulou-Stamati et al., reported that PFCs are one of the endocrine disruptors in cosmetics[6]. Perfluorinated carboxylic acids (PFCAs) were detected from Japanese cosmetics (total PFCAs concentration of foundation: N.D.-5.900 ng/g-wet and sunscreen: N.D.-19,000 ng/g-wet)[7]. ECHA pointed that cosmetics in European market contain PFOA and related substances[8] while occurrence of PFCs in cosmetics in worldwide is not well known. Cosmetics contain the ingredients which are suspected as precursors of PFCs, such as C9-15 fluoroalcohol phosphate, DEA perfluoroalkyl phosphate and Perfluorooctyltrietoxysilan. Jessica et al., predicted[5] that the concentration of PFOA from a phosphoric precursor in human serum will increase from 2000 to 2020. However, it is difficult to analyze each of precursors because they are various and their standard chemicals are limited. Our research group suggested a method, which evaluate PFC formation potentials (PFC-FPs) defined as PFCs amount formed from precursors[9]. The concept of PFC-FPs is shown in **Figure 1**. It uses oxidative conversion of precursors to PFCs under a certain condition. Main objective of this study was to understand occurrence of PFCs and their formation potentials in cosmetics in Asian and European countries. In addition, time-of-flight-mass spectrometry (TOF-MS) was applied to examine precursors.

2. Materials and methods

2.1 Prepareation of samples

Cosmetic samples used in this study were purchased in Japan, Thailand, and Italy, from December 2015 to March 2016. The samples such as Liquid/Powder foundation, Makeup base, Sunscreen, Lip rouge and Manicure, were 31 products in 15 kinds of company. The list of samples is shown in **Table 1**. Most of cosmetics list any fluorinated ingredients in their labels.

2.2 Pre-treatment

Basically, 100 mg cosmetic samples and 10 mL of methanol(MeOH) were placed in polypropylene (PP) tube and mixed for 3h.

<PFCs> Firstly, 1 mL of sample and recovery surrogate (1 ng each of $_{13}C_2$-labeled PFHxA, $_{13}C_4$-labeled PFOA, $_{13}C_4$-labeled PFDA, $_{13}C_4$-labeled PFOS in MeOH) were added to a new PP tube. Then, 1 mL of 0.5M tetrabutylammonium/0.25 M sodium carbonate buffer solution (pH was adjusted to 10) and methyl tert-butyl ether (MTBE) were added to the sample, and the tubes were vortexed for 60s. After this, the samples were centrifuged at 3,000 rpm for 5 min. About 3 mL supernatant solution was transferred to a new PP tube and 3 mL new MTBE was added. These steps were repeated. The total 6 mL solution exchange to 3 mL MeOH without dryness while N_2 gas purge. 3 mL MeOH was added to it two times at the same condition. After that, extracts were mixed and passed through 0.2 μm syringe filter (Whatman®) and Envi-carb cartridge (Supelco) to remove matrix substances. The final sample volume is 5 mL.

<PFC-FPs> Firstly, 1 mL of sample, the recovery surrogate and 250 mL Milli-Q water (PFCs-free) were added to 250 mL bottle made by PPCO. After that, $K_2S_2O_8$ (60 mM) and NaOH (150 mM) were

added and heated for 24 hours under 95°C condition[9]. Samples (250 mL) which the recovery surrogate was added were extracted by solid phase extraction (SPE) passing through an Oasis® WAX cartridge (Waters). After this, the cartridge was dewatered by centrifugation at 2,000 rpm for 4 min. PFCs eluted with 2 mL MeOH and 3 mL MeOH in 1% NH_4OH solution. After that, cleanup is the same method as pre-treatment. The final sample volume is 5 mL.

2.3 Instrumental Analysis and Quantification

12 PFCAs (C4-14, 16) and 3 perfluoroalkyl sulfonate (PFASs) (C4, 6, 8) were analyzed by LC-MS/MS (Agilent). Unknown precursors were examined between m/z 80 to m/z 1,700 by LC-TOF-MS (Agilent). Details of separation and quantification about the instrument were explained in a previous publication[9]. Instrumental Detection Limit was 0.01-0.03 ng/mL, Instrumental Quantification limit was 0.02-0.09 ng/mL. Recovery rates were ranged between 78-105%, and standard deviations of recovery value for samples were less than 30%. The concentrations of PFC-FPs were calculated as the difference those of PFCs before and after oxidative conversion.

3. Results and discussion

3.1 Concentrations of PFCs and their formation potentials in cosmetics

Total concentrations of 15 PFCs and their formation potentials (PFC-FPs) in cosmetics were shown in **Figure 2**. In case of PFCs, their concentrations ranged from 245 to 8,170 ng/g-wet in their liquid/ powder foundations and makeup base, 202-1,660 ng/g-wet in their lip rouge and manicure. PFC-FPs concentrations ranged from 6 to 93,200 ng/g-wet. In some foundations and makeup bases, their concentrations of PFC-FPs were 11-49 times higher than those of PFCs. There were no significant differences in PFCs and PFC-FPs concentrations among 6 countries.

3.2 Concentrations of PFOA and PFOA-FP in cosmetics

Concentrations of PFOA and PFOA-FP in cosmetics containing different ingredients are shown in **Figure 3**. PFOA and PFOA-FP were detected in some cosmetics containing ingredients which are "C9-15 fluoroalcohol phosphate", "C8-18 fluoroalcohol phosphate", "C4-14 perfluoroalkylethoxy dimethicone", and "DEA perfluoroalkyl phosphate". PFOA and PFOA-FP were not detected in almost all cosmetics with other ingredients or no fluorinated ingredient.

3.3 Concentrations of PFCA and PFCA-FPs with different carbon chain length

Concentrations of PFCAs and PFCA-FPs with different carbon chain length in two cosmetics (made in Thailand and France) containing "C9-15 fluoroalcohol phosphate" are shown in **Figure 4**. The concentrations of PFCAs with even carbon chain length (C6, 8, 10) were higher than that of PFCAs with odd carbon chain length (C5, 7, 9, 11). The detected concentration of all PFCA-FPs ranged from N.A. (not available) to 1,550 ng/g-wet. Long chain PFCAs (C8 or longer carbon chain) and PFCA-FPs were detected in some cosmetics. Therefore, it suggested that the cosmetics with the ingredients contained precusors which form PFCAs.

3.4 Examination on chemical structure of precursors

LC-TOF-MS was applied to examine structure of precursors in a powder foundation (JPN3) contained "C9-15 fluoroalcohol phosphate". Detected chromatograms of each m/z were shown in **Figure 5**. Seven kinds of polyfluoroalkyl phosphate ester (PAPs), namely, 6:2monoPAP, 8:2 monoPAP, 10:2monoPAP, 6:2diPAP, 7:2diPAP, 8:2diPAP, 9:2diPAP were detected. These chemical substances were suspected to form PFCAs.

In Asian and European countries, some cosmetics with specific fluorinated ingredients (e.g. C9-15 fluoroalcohol phosphate) contained PFCs and their precursors which form them.

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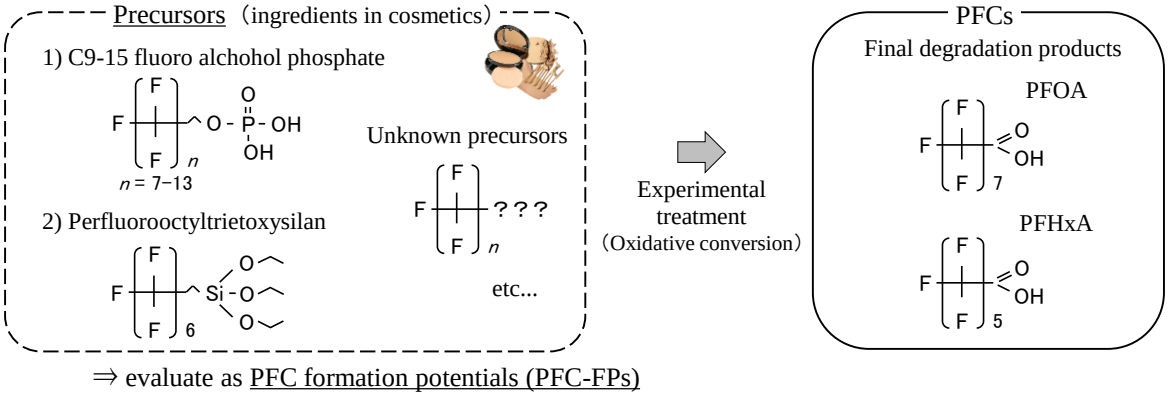

Figure 1 Concept of PFC formation potentials (PFC-FPs)

Table 1 The list of cosmetic samples

ID	Type of Cosmetics	Fluorinated ingredients	Country
JPN1	Liquid foundation	C4-14 perfluoro alkylethoxy dimethicone, C8-18 fluoroalcohol phosphate	Japan
JPN2	Liquid foundation	DEA perfluoroalkyl phospate	Japan
JPN3	Powder foundation	C9-15 fluoroalcohol phosphate	Japan
JPN4	Powder foundation	C8-18 fluoroalcohol phosphate	Japan
JPN5	Makeup base	C9-15 fluoroalcohol phosphate	Japan
JPN6	Makeup base	DEA perfluoroalkyl phospate	Japan
JPN7	Lip rouge	Perfluorooctyltrietoxysilan	Japan
JPN8	Lip rouge	Perfluorooctyltrietoxysilan	Japan
JPN9	Manicure	DEA perfluoroalkyl phospate	Japan
THA1	Powder foundation	C9-15 fluoroalcohol phosphate	Thailand
THA2	Powder foundation	C9-15 fluoroalcohol phosphate	Thailand
THA3	Powder foundation	C9-15 fluoroalcohol phosphate	Thailand
THA4	Powder foundation	C9-15 fluoroalcohol phosphate	Thailand
THA5	Powder foundation	C9-15 fluoroalcohol phosphate	Thailand
THA6	Makeup base	C9-15 fluoroalcohol phosphate	Thailand
THA7	Makeup base	—	Thailand
THA8	Sunscreen	C9-15 fluoroalcohol phosphate	Thailand
THA9	Sunscreen	C9-15 fluoroalcohol phosphate	Thailand
IDN1	Sunscreen	C9-15 fluoroalcohol phosphate	Indonesia
IDN2	Sunscreen	—	Indonesia
FRA1	Liquid foundation	Syntheticfluorphlogopite	France
FRA2	Powder foundation	—	France
FRA3	Makeup base	C9-15 fluoroalcohol phosphates C9-15 fluoroalcohol phosphate	France
FRA4	Makeup base	—	France
FRA5	Lip rouge	Syntheticfluorphlogopite	France
FRA6	Manicure	Syntheticfluorphlogopite	France
FRA7	Manicure	perfluorodecalin	France
ITA1	Liquid foundation	Syntheticfluorphlogopite	Italy
ITA2	Powder foundation	Polyperfluoroethoxymethoxy difluoroethyl peg phospate	Italy
ITA3	Makeup base	—	Italy
MCO1	Sunscreen	—	Monaco

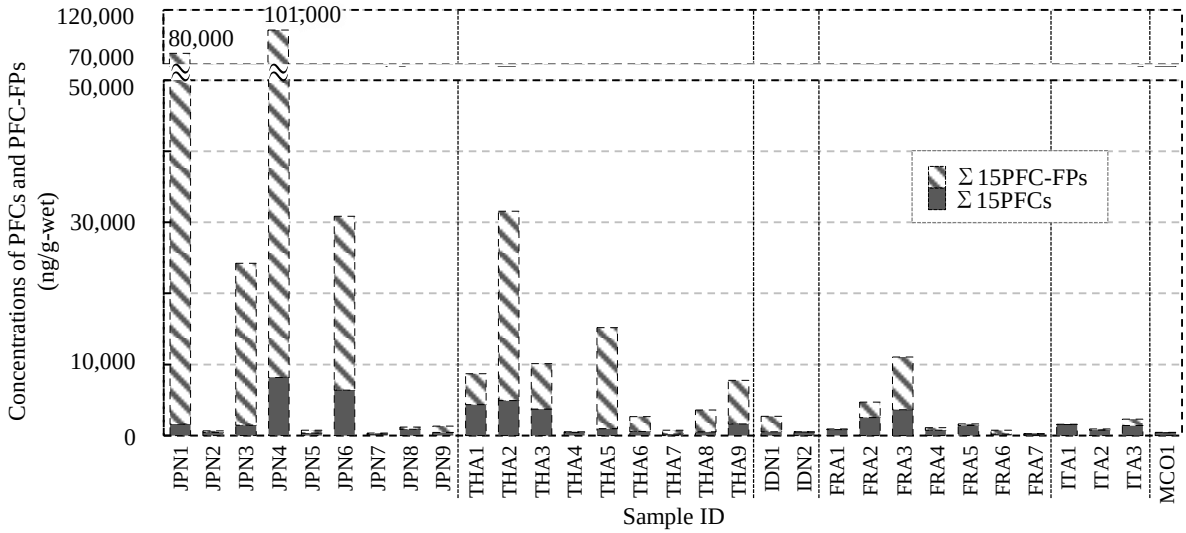

Figure 2 Concentrations of 15 PFCs and thier formation potentials

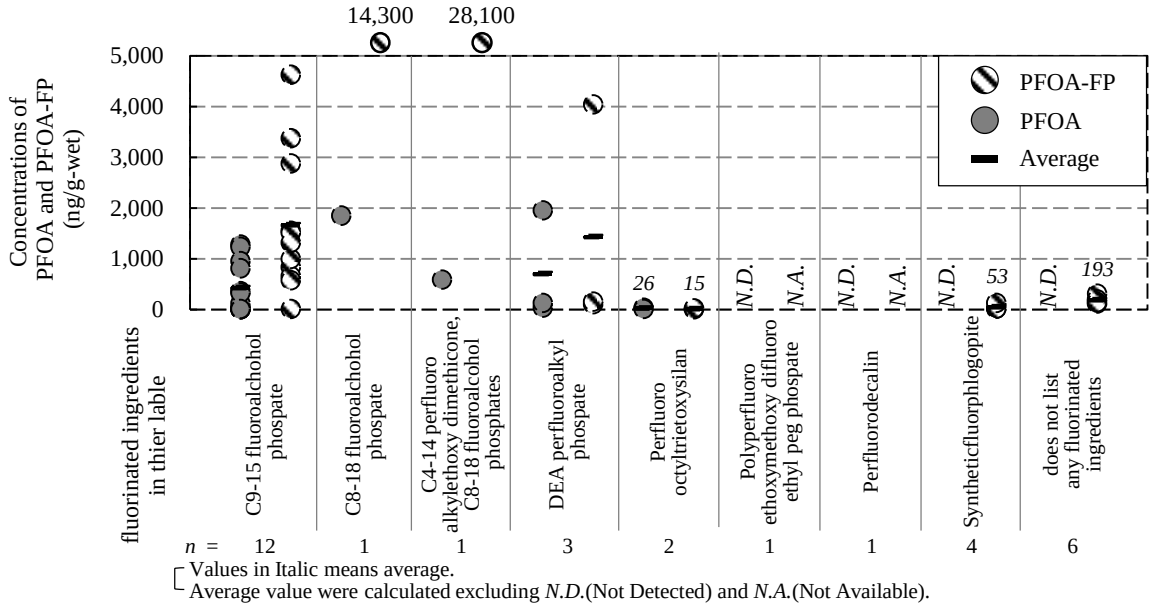

Figure 3 Concentrations of PFOA and PFOA-FP in cosmetics contained different ingredients

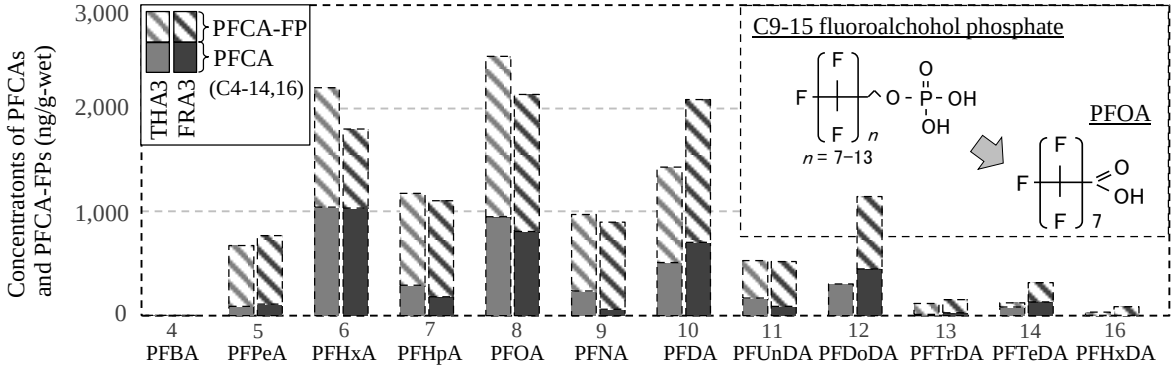

Figure 4 Concentrations of PFCA formation potentials with different carbon chain length

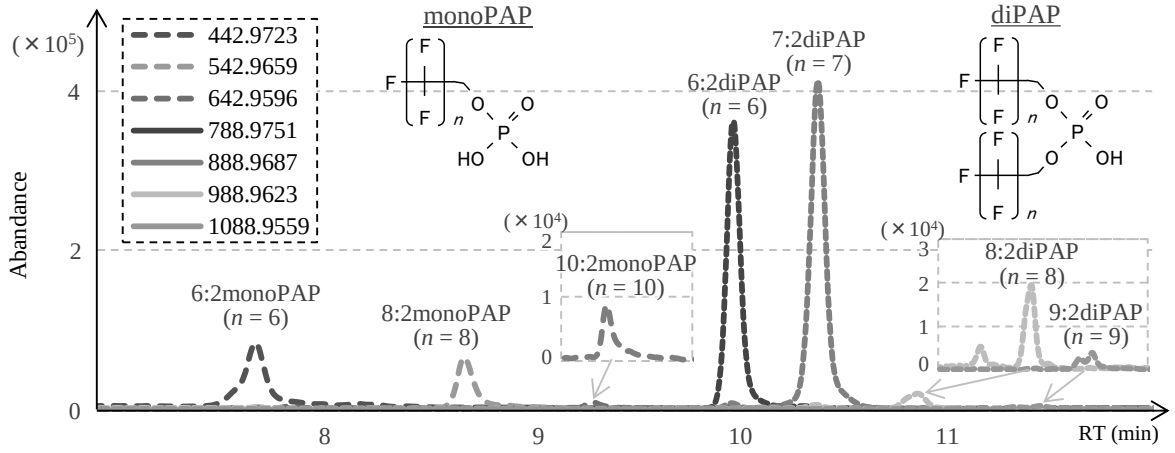

Figure 5 Chromatograms of polyfluoroalkyl phosphate esters (PAPs)