STUDY ON EXTRACTION METHOD OF DIOXINS AND PERFLUORINATED ORGANIC COMPOUNDS (PFOS/PFOA) IN AIR BY USE OF PRESSURIZED SOLVENT EXTRACTION (PSE)

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Introduction

Dioxins are one of the hazardous chemicals which are regulated in the lowest level globally. Much work is required for the pretreatment methodincluding extraction, purification and condensationprior to GC/MS analysis.[1)]The extraction processto extract dioxins from samples uses organic solvents. It is necessary to have an effective reproducible extraction method to analyze samples accurately and precisely. Today, many laboratories adopttheSoxhletmethodto extract lipids from samples.[2)3)] Although it shows good extraction efficiency, it takes more than 16 hours and it involves safety hazards such as a fire or solvent burnswhen handling organic solvent at a high temperatures.

High pressure fluid extraction such as pressurized solvent extraction (PSE)[4)] or accelerated solvent Extraction (ASE)[5)] can be automated to include theSoxhletprocess and shorten extraction timestotwo hours.Theseextraction methodsarelisted in the manuals on determination of dioxins in "sediment"[6)], "soil"[7)], "gas emissions, ash and certain cinders"[8)], therefore many organizations use them.Thereare also a few examples which indicated this technique for air samples.

The Japanese analysis manual of atmospheric dioxins describes that "other extracting methods may be used after carrying out a comparison examination withtheSoxhlet method and its validity is confirmed"[9)]. Therefore we have investigated whether PSE can be used for dioxins analysis in air. In addition, investigations between PSE and SoxhletforPerfluorooctanesulfonic acid (PFOS) and Perfluorooctanoic acid (PFOA) have been carried out.

Materials and methods

<Dioxins>

Target substances of dioxins are 4-8 Polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDDs/PCDFs) and 12 types of non-ortho and mono-ortho coplanar-PCBs (Co-PCBs). The sampling used two units of high volume air samplers (HV-700F, SIBATA, Tokyo, Japan) which were attached to quartz fiber filter papers (QFF) and polyurethane foams (PUF) on the roof of the Osaka City Institute of Public Health and Environmental Sciencesduring June 2012.The two devices were run in parallel for 3days continuously with a sampling flow rate of 700L/min, resulting in approximately 1,000m^{3}over 24h. QFF and PUF were put into aluminum coated PP bags after sampling and preserved at -20^{o}Cuntil extracted.

Two extraction methods were evaluated; manual Soxhletextraction and PSE (SpeedExtractor E-914, BUCHI). Dioxins were extracted by Soxhlet extraction and PSE from two sets of QFF and PUF which had sampled air at the same place at the same time. For the Soxhlet method toluene was used toextract both QFF and PUF for 24 hours.The extract conditionsused for PSE are shown (Table.1). After labeled clean-up spikes 2,3,7,8-Te~HpCDD/Fs 1ng, OCDD/F 2ng and 12 types of Co-PCBs 2ng (DF-LCS-A and PCB-LCS-A, Wellington) were added into each extracted sample, various clean-ups, such as multilayer silica gel chromatography and activated carbon silica gel column chromatography, were applied. The final volume

Table 1 Extraction Method of DXN using PSE (QFF, PUF)

Parameter		QFF	PUF
Temperature		100 °C	80 °C
Pressure		10MPa	10MPa
Vial		240 mL	240 mL
Cell		40 mL	120 mL
Solvent			
	Type	Toluene	Toluene
	Ratio	100%	100%
Number of Cycles		3	3
Cycles			
	Heat-up (min)	3»1 » 1	3»1 » 1
	Hold (min)	3»3»3	3»3»3
	Discharge (min)	3» 3»3	3» 3»3
Flush with Solvent		2 min	3 min
Flush with Gas		6 min	6 min

was100μL, with syringe spikes (DF-IS-I and CB-IS-B, Wellington). The dioxin quantitation and identification were determined by HRGC/HRMS (JMS-800D, JEOL) with a resolution of 10,000.

Table 2 Extraction Method of PFOS/PFOA using PSE (QFF, PUF, ACF)

Parameter		QFF	PUF	ACF
Temperature		80 °C	80 °C	80 °C
Pressure		10 MPa	10 MPa	10 MPa
Vial		240 mL	240 mL	240 mL
Cell		40 mL	120 mL	40 mL
Solvent				
	Type	Acetone	Acetone	Acetone
	Ratio	100%	100%	100%
Number of Cycles		3	3	3
Cycles				
	Heat-up (min)	3»1 » 1	3»1 » 1	3»1 » 1
	Hold (min)	3»3»3	3»3»3	3»3»3
	Discharge (min)	3» 3»3	3» 3»3	3» 3»3
Flush with Solvent		2 min	3 min	2 min
Flush with Gas		6 min	6 min	6 min

<PFOS/PFOA>

The sampling used two units of high volume air samplers(HV-700F, SIBATA, Tokyo, Japan) on the roof of the Osaka City Institute of Public Health and Environmental Sciences during June 2012. The two devices were run in parallel for 3days continuously with a sampling flow rate of700L/min resulting in approximately 1,000m^3over 24 h. The trapping materials used activated carbon fiber filter paper (ACF),QFF and PUF. After sampling the preservation of QFF, PUF and ACF was similar to the dioxins method. Both Soxhlet extraction and PSE were carried out in duplicateoneach of the trapping materials. For the Soxhlet method acetonewas used to extract the QFF, PUF and ACF for 24 h. The extractionconditionsused for PSE are shown (Table2). 2ng of isotope-labeled PFOS and PFOA(MPFAC-MXA, Wellington) were added into each extracted sample as clean-up spikes.Following evaporation, using a rotary evaporator, to 5ml and clean-up using a solid phase extraction cartridge (OASIS WAX, Waters) the target substances were eluted with 4ml aqueous ammonia/methanol (1/999). After concentration using the nitrogen gas, the final volume was 1ml, with syringe spikes isotope-labeled PFOS/PFOA (CUS-MPFC-SS1+$^{13}C_8$PFOS, Wellington). Its quantitation and identification were determined by LC/(-)ESI-MS/MS(Xevo TQ MS, Waters).

Results and discussion

Chemical compounds in this investigation are 9-isomers of PCDDs, 11-isomers of PCDFs, 12-isomers of Co-PCBs and PFOS/PFOA. The comparison of the results of the Soxhletextraction and PSE are shown in Fig.1 for dioxins and in Fig.2 for PFOS/PFOA. The recovery rate for dioxins is 56-120% and for PFOS/PFOA is 44-110%.

<Dioxins>

PCDDs are within 24%, PCDFs 11-isomersare within 17% and Co-PCBs 12-isomersare within 23%, using the meanisomer measurements we verified all isomers within 30%. The results of this investigation have shown, (although we must validate in other seasons),thatPSE has comparable extraction efficiency to Soxhletextraction.

<PFOS/PFOA>

The results of similar investigations for PFOS/PFOA show that PFOS is within 26% and PFOA is within 59% to the mean. We obtain good results for PFOS as well as dioxins, buttheband is larger for PFOA. The PSE results of all three samples are lower than that of the Soxhletextraction, this maybe due to the chosen extraction solvent. Further investigation for compounds having various physicochemical properties and the modification of the extraction conditions may increase the use of PSE.

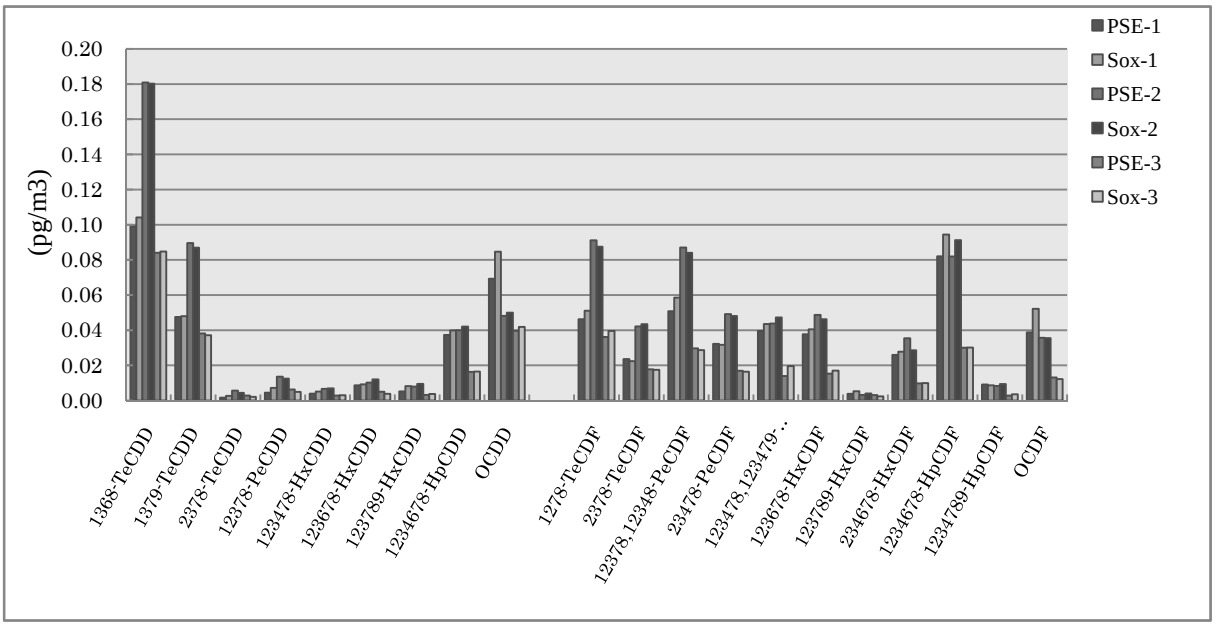

Fig 1. Comparison of PCDD/Fs concentrations using PSE and Soxhlet Extraction

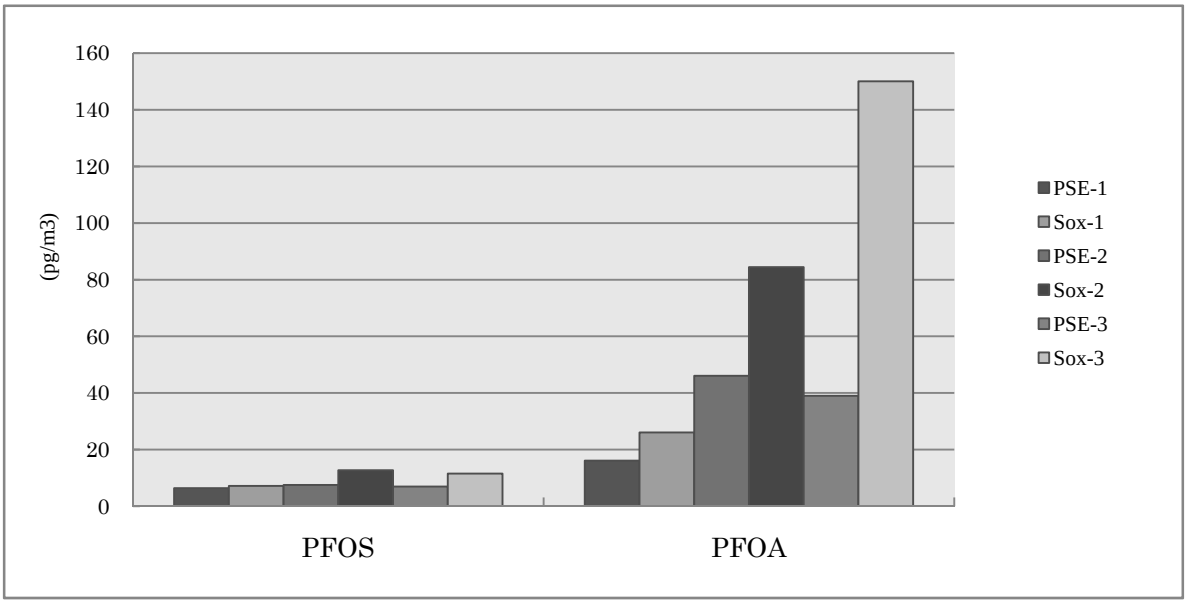

Fig.2 Comparison of PFOS/PFOA concentrations using PSE and Soxhlet Extraction

References

1) US EPA Method 1613, (1994), http://water.epa.gov/scitech/methods/cwa/organics/dioxins/upload/2007_07_10_methods_method_dioxins_1613.pdf
2) Japanese Industrial Standards Committee, JISK0311, 2008
3) Japanese Industrial Standards Committee, JISK0312, 2008
4) BUCHI, http://www.buchi.com/
5) Thermo Fisher Scientific (Dionex), http://www.dionex.com/en-us/index.html

6) Ministry of the Environment, Japan (2009),
http://www.env.go.jp/chemi/dioxin/manual/teishitsu-smp/main.pdf (in Japanese)
7) Ministry of the Environment, Japan (2009),
http://www.env.go.jp/chemi/dioxin/manual/dojo_smm-manual/main.pdf (in Japanese)
8) Ministry of the Environment, Japan (2010),
http://www.env.go.jp/chemi/dioxin/manual/edr_sim-method/ia_manual.pdf (in Japanese)
9) Ministry of the Environment, Japan (2008), http://www.env.go.jp/air/osen/manual/manual.pdf (in Japanese)