# Concentration of UPOPs (PCDDs, PCDFs, Co-PCBs, HCB) with the various sampling methods in ambient air 

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## Introduction

Recently, there is a large consideration on the multiform hazardous substance such as PCCDs, PCDFs, PCBs, and HCB called UPOPs in the global. Therefore, the concentration of UPOPs in the ambient air, emitted from specific stationary sources of the industrial complex, is analyzed frequently and their toxicities are also evaluated for the health of resident and for the safety of environment. In many countries the high volume air sampler is used for the sampling of the hazardous substance within the ambient air. In addition, the sampling conditions, i.e., flow rate and adsorption materials for the sampling of UPOPs, are a little bit different, which is originated from the slight difference in the physicochemical properties of UPOPs. Such a situation leads us to find out either the new or the modified sampling method for the analysis of UPOPs. Here, we have investigated the effects of the sampling methods on the concentration of UPOPs. We have also evaluated both the confidence and accuracy of the methods employed in this study. It is worthwhile to point out that the confirmed method in this study will be suggested as the Korean official sampling method of UPOPs.

## Materials and Methods

Intentionally PCDDs, PCDFs, Co-PCBs and HCB as UPOPs are sampled simultaneously in this study, in which the flow rate and the adsorption material were changed by each sampling. The high volume air sampler was used for sampling UPOPs in ambient air, where the sampling time was 24 hours. The sampling flow rates of UPOPs were $700 \mathrm{ml} / \mathrm{min}$ and $225 \mathrm{ml} / \mathrm{min}$. Quartz filter (QF) as an adsorption material was used for the particle phase of UPOPs, while poly urethane form(PUF), XAD-2 resin and activated carbon paper filter(ACPF) were for the gaseous phase of UPOs. We have employed three different methods; the first method consists of $700 \mathrm{ml} / \mathrm{min}$ of flow rate and $\mathrm{QF}+\mathrm{PUF}+\mathrm{XAD}-2$ resin +PUF of the adsorption materials, the second consists of $225 \mathrm{ml} / \mathrm{min}$ and $\mathrm{QF}+\mathrm{PUF}+\mathrm{XAD}-2$ resin $+\mathrm{PUF}^{1}$, the last

## Sample preparation and analysis

one consists of $700 \mathrm{ml} / \mathrm{min}$ of flow rate and $\mathrm{QF}+\mathrm{PUF}+\mathrm{ACPF}+\mathrm{PUF}^{1,2}$. The samples were collected for three days with each method at the same point from the industrial complex located in western Korea in February. The analysis of UPOPs was performed by HRGC/HRMS, where the column SP 2331 and DB5-MS were used for the separation of PCDDs/PCDFs and Co-PCBs/HCB, respectively. The collected samples were extracted by soxhlet with toluene during the 16-18 hrs. The multi-silicagel clean up according to JIS method ${ }^{3}$ was used for PCDDs/PCDFs, Co-PCBs and HCB and also for the PCDDs/PCDFs alumina clean up was used after mult-silicagel clean up.

## Results and Discussion

Before collecting samples, the standard materials( ${ }^{37} \mathrm{Cl}_{4}$-TCDD for PCDDs/PCDF / ${ }^{13} \mathrm{C}_{12}-2,4,4^{\prime}$ - TriCB, ${ }^{13} \mathrm{C}_{12}-2,3,3^{\prime}, 5,5$ '-PentaCB and ${ }^{13} \mathrm{C}_{12}-2,2^{\prime}, 3,3^{\prime}, 5,5^{\prime}, 6-$ HeptaCB for $\left.\mathrm{Co}-\mathrm{PCBs}\right)^{4,5}$ were spiked into the adsorption materials to the comparison with the sampling methods. For the PCDDs/PCDFs, the first method ( $700 \mathrm{ml} / \mathrm{min}$ and $\mathrm{QF}+\mathrm{PUF}+\mathrm{XAD}-2$ resin+ PUF) showed the highest recovery efficiency of standard as well as the highest concentration of sample. For the Co-PCBs, the second method ( $225 \mathrm{ml} / \mathrm{min}$ and QF+PUF+XAD-2 resin+ PUF) gave the highest recovery standard and the highest concentration of sample. For the HCB , the third method ( $700 \mathrm{ml} / \mathrm{min}$ and $\mathrm{QF}+\mathrm{PUF}+\mathrm{ACPF}+\mathrm{PUF}$ ) showed the highest concentration of sample. The recovery efficiencies of labeled compound stock solution of PCDDs/PCDF and Co-PCBs are found to be $75-90 \%$ and $100-121 \%$, respectively, while that of HCB is observed to be only $37-46 \%$. The very low recovery efficiency of HCB seems to be attributed to the usage of toluene as an extractor by soxhlet. Based on our observation, the dichloromethane ${ }^{8}$ or diethylether in hexane ${ }^{7}$ as an extractor may be suitable for HCB. In the case of PCDDs/PCDFs and Co-PCBs there is no problem to use toluene and also the mult-silicagel clean up according to JIS method. In this regard, dichloromethane as an extractor appears to be applicable for the simultaneous extraction of the PCDDs, PCDFs, Co-PCB and HCB. In some previous studies ${ }^{6,9,10}$, the XAD-2 resin was suggested as the proper adsorption material and below $500 \mathrm{ml} / \mathrm{min}$ as the proper flow rate for the collection of HCB in ambient air. Therefore, it is concluded that the third method used in this study, still showing the highest concentration, is not the proper way of sampling HCB and the second method is suitable for the simultaneous collection of UPOPs sample in the ambient air.

Tables 1, 2 and 3 show the recovery of standard and concentration of samples with the various sampling methods.

Table 1. The recovery of standard and concentration of samples with first method

| Items | PCDDs/PCDFs | Co-PCBs | HCB |
| :--- | :--- | :--- | :--- |
| Clean up standard (\%) | 90.9 | 76.59 | - |
| Labeled compound stock solution (\%) | 72.5 | 104.85 | 37.2 |


| Concentration(pg-TEQ/Sm ${ }^{3}$ ) | 0.262 | 0.018 | 0.19 |
| :--- | :--- | :--- | :--- |

Note : average value of three times

Table 2. The recovery of standard and concentration of samples with second method

| Items | PCDDs/PCDFs | Co-PCBs | HCB |
| :--- | :--- | :--- | :--- |
| Clean up standard (\%) | 86.8 | 89.17 | - |
| Labeled compound stock solution (\%) | 84.6 | 108.64 | 45.7 |
| Concentration(pg-TEQ/Sm ${ }^{3}$ ) | 0.232 | 0.028 | 0.36 |

Note : average value of three times

Table 3. The recovery of standard and concentration of samples with third method

| Items | PCDDs/PCDFs | Co-PCBs | HCB |
| :--- | :--- | :--- | :--- |
| Clean up standard (\%) | 84.2 | 86.51 | - |
| Labeled compound stock solution (\%) | 83.4 | 101.27 | 36.2 |
| Concentration(pg-TEQ/Sm ${ }^{3}$ ) | 0.114 | 0.013 | 0.94 |

Note : average value of three times

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