

Measurement of emission flux of hydrogen chloride from damaged PVC materials by Passive Flux Sampler

(パッシブ・フラックス・サンプラーによる劣化した塩化ビニル製品からの塩化水素放出量の測定)

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1. Introduction

Nowadays, polyvinylchloride (PVC) is an essential material for daily household and industrial uses. However, the PVC is not robust to environmental factors such as heat and light which trigger thermal and/or photo degradation with dehydrochlorination from the polymer. In this study, we have developed Passive Flux Sampler (PFS) which can collect hydrogen chloride(HCl) in passive mode, and applied to measurements of emission flux of HCl from damaged PVC materials.

2. Experimental

2.1 Passive Flux Sampler

Fig.1 shows a schematic view of the PFS. The sampler simply consist of a circular stainless Petri dish, PTFE disk, trapping filter and PTFE O-ring. The sampler was tightly put on the surface of the PVC materials. The trapping filter was fixed by O-ring to keep a constant distance (diffusion length) from the surface of test pieces.

2.2 Preparation of trapping filter

Firstly, chromatographic grade filter paper (Advantec, No.590, 47mm) was soaked in 2%-H₂O₂ for one hour, washed by ion-exchange water and then dried in vacuum desiccators all day long to reduce a background level of chloride ion. Afterwards, three pieces of the filter were multiplied and dipped in 50%triethanolamine/10%glycerol aqueous solution. The trio was then put on the PTFE plate and dried in desiccators, to give a trapping filter for HCl.

2.3 Analytical method

After sampling, the trapping filter was transferred to a test tube. The collected HCl was extracted in 25ml of ion-exchange water with vigorous shaking for 30 minutes. The extract was then filtered through hydrophilic filter paper (Millex LH25, 0.45 μm). The residual filter was extracted again by another 25mL of water and the filtrates were combined. Chloride ion in the 50ml extract was determined by ion chromatography(Dionex ICS-90). The collection amount of HCl was converted to emission flux from the PVC materials by equation .

$$E = \frac{W}{s \cdot t} \dots \left(\begin{array}{l} E \text{ (mg/cm}^2\text{h):emission flux} \quad W \text{ (}\mu\text{g):collection amount} \\ s \text{ (m}^2\text{):cross-section of the stainless petri dish} \quad t \text{ (h):sampling time} \end{array} \right)$$

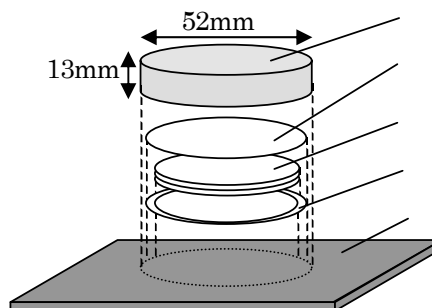


Fig.1 Schematic view of the PFS
Stainless Petri Dish PTFE plate
50%TEA/10%Glycerol impregnated filter
O-ring(PTFE) PVC materials

3. Results and Discussion

3.1 Measurement of emission flux of HCl from PVC materials

The emission fluxes of HCl from the commercially available PVC, measured by the PFS method, are shown in Table 1. The emission fluxes of the initial PVC materials (no treatment) were very low. However, combination of hard PVC boards with adhesives enhanced the emission of HCl (Treatment). As well as, wiping the surface of PVC materials also caused an increase of emission flux of HCl in all types of materials. Thermal dehydrochlorination was found in the heated materials which stand near infrared heater. These results show that emission flux of HCl is very sensitive to external stimulus given to the PVC materials in our daily life.

Table1 Emission flux of HCl from marketed PVC materials (n=3,40 ,L=0.3cm)

Sample	Emission flux of HCl(mg/m ² /h)			
	Virgin	Treatment	Ethanol wiping	Heating
Hard PVC board	0.16±0.002	0.43±0.1	0.2±0.002	0.12±0.006
Wallpaper	< 0.02	< 0.01	0.46±0.04	0.33±0.01
Wrap film	0.09±0.008	—	0.39±0.04	0.23±0.02
Plastic bag	0.18±0.03	—	0.32±0.03	0.27±0.008

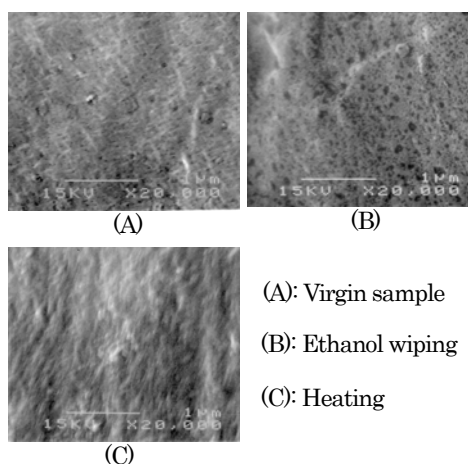
Detection limit:3 B

3.2 Mechanism of HCl emission from PVC materials

Fig.3 shows SEM images of the surface of plastic bag with and without treatments. The treated PVC materials (B and C) had relatively rough surfaces. The increased surface areas probably contributed increases in emission fluxes of HCl. Fig.4 shows influence of diffusion length on the collection amount of HCl in the ethanol-treated samples of hard PVC board and wallpaper. No dependence was found in the thick hard board. This means diffusion process of HCl in a solid phase is rate-determining step of the HCl emission from the hard board. On the contrary, relatively thin materials such as wallpaper, molecular diffusion in a gas phase determines the overall rate of the emission, and thus the emission flux proportionally increased with a converse of diffusion length in the PFS, as suggested by Fick's law.

4. Conclusion

Passive flux sampler was successfully applied to the determination of emission flux of HCl from commercially available PVC products. The greater emission fluxes were found in the damaged samples. This simple measurement also provided information of the emission mechanism of HCl which determines overall flux from the surface of the PVC materials.



(A): Virgin sample
(B): Ethanol wiping
(C): Heating

Fig.3 Observation of surface of Plastic bag by SEM

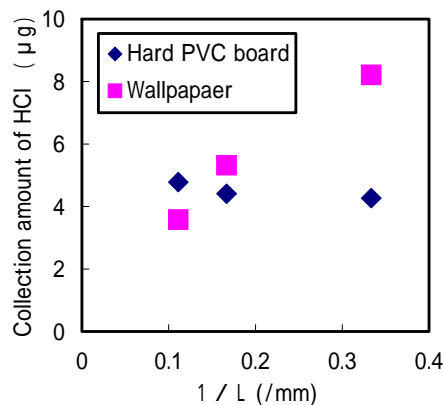


Fig.4 Collection amount of HCl versus converse of diffusion length (Ethanol wiping,40)