DETECTION OF POLY HALOGENATED BIPHENYLS IN THE $FeCl_3$ MANUFACTURING PROCESS

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Abstract

Co-PCB and Co-PXB (Polyhalogenated Biphenyls) have been detected as contaminants in the production of $FeCl_3$. Relative PCB concentrations were #126 > #169 > #189. Monobromo congeners of Co-PCB #126, #169 and #189 were also detected. The concentration order of Monobromo biphenyl that replaced Cl with Br of Co-PCB was #126 ≒ #169 > #189. The concentration order was #126 (pentachloro biphenyl) > #126 (Monobromo-Tetrachloro Biphenyl) > #126 (DibromoTrichloro Biphenyl). Tribromo substituted Biphenyls were not detected. PBrDPE in the printed circuit board might be decomposed to polybromophenol and polybromobenzene radical in strongly acidic solution in the presence of HCl, $FeCl_2$ and $CuCl_2$. Dimerization of polybromobenzene radical forms Co-PXB with selective debromination and Br-Cl substitution.

Introduction

Liquid $FeCl_3$ used for coagulating sedimentation in wastewater treatment is recycled, and at the same time copper and nickel are recovered, using etching liquid of printed circuit board from etching facility and waste acid from steel mills. Though limited to specific product lots, liquid $FeCl_3$ produced during a certain period have contained high concentrations of PCB and PXB. The congener distribution characteristics of PCB and PXB contamination in liquid $FeCl_3$ was found, and the formation process was newly deduced.

Materials and Methods

GC/MS analysis : The analysis was carried out using a HP 6890 gas chromatograph connected to a JMS-800D mass spectrometer (JEOL Ltd. Japan) operating at a resolution >10 000. Co-PCB, Co-PXB and PXDF were analyzed using HT8-PCB column. Temperature program used for congener specific separation of the PCB, PXB and PXDF on HT8-PCB column: 120C, 20C/min. to 180° C, 2C/min. to 260C. 5C/min. to 300C, 5 min. isothermal. Monitoring ions for GC/MS analysis are listed in Table 1.

Standards: Commercially-available native/labeled standards were obtained from CIL as authentic standard/mixtures for crosschecking the assignment. , 4'-bromo- 3, 3', 4, 5-tetrachloro biphenyl was obtained from CIL for a PXB standard.

Fluorescent X-ray analysis: X-ray tube: Vertical rhodium tube, X-ray output: 50 kV – 60 mA, Measured elements: 22Ti ~ 92U (Excluding Hg), Analyzing crystals: LiF and Ge, Detector: Scintillation counter, Effective beam width: 35 mmØ, Sample holder: Hollow aluminum holder for filter, An intravenous filter was set in a 47 mmØ open plastic filter holder and 2 ~ 5 ml of liquid sample was dropped on the filter. After drying for a minimum 5 hr at 65°C, the strength of these filters was measured at the fluorescent X-ray spectral wavelengths proper to the various heavy metal elements.

Results and Discussion

Figure 1 shows the GC/MS-SIM chromatogram of the contaminated liquid $FeCl_3$. Monobromo #126, #169 and #189 were detected. PCB concentration was #126 > #169 > #189. The relative concentrations of monobromo compounds that replaced Cl with Br was #126 ≒ #169 > #189. Figure 2 is the GC/MS-SIM chromatogram of Co-PXB. The concentration level was #126 (PeCB) > #126 (MBrTeCB) > #126 (DiBrTrCB), and Tribromo, Tetrabromo and others were not detected. Among MBrTeCB; 3,3',4,4,5' -monobromo-tetrachloro biphenyl, only 4'-bromo- 3,3',4,5-tetrachloro biphenyl is commercially available. In Figure 2, #126 (MBrTeCB) was proposed to be 3'-bromo-3,4,4',5-tetrachloro biphenyl, 3'-bromo-3,4,4',5'-tetrachloro biphenyl, or 4'-bromo-3,3',4,5'-tetrachloro biphenyl.

Table 1 Monitoring ions for GC/MS analysis (PXB, PXDF)

PeCB: 325.8805, 327.8775	BrTrCB: 333.8718, 335.8694
^{13}C-PeCB: 337.9200, 339.9178	BrTeCB: 367.8329, 369.8303
MBrTeCB : 367.8329, 369.8303	BrPeCB: 403.7913, 405.7886
DiBrTrCB : 413.7800, 415.7770	BrHxCB: 437.7523, 439.7496
TrBrDiCB: 457.7297, 459.7274	BrTrCDF : 349.8487, 351.8460
TeBr4MCB: 501.6792, 503.6771	BrTeCDF : 383.8096, 385.8070
PeBrBiphenyl: 547.6268, 549.6247	BrPeCDF: 417.7706, 419.7679

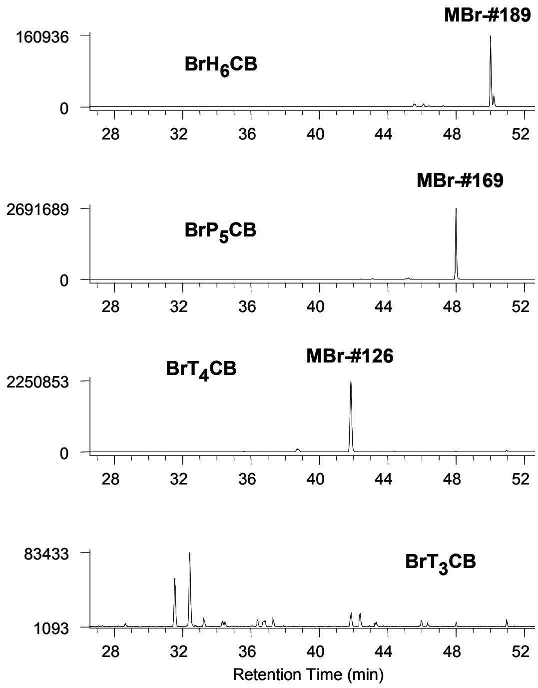


Figure 1 GC/MS chromatogram in contaminated $FeCl_3$
Co-PXB: #126,#169,#189 (monobromo substituted)

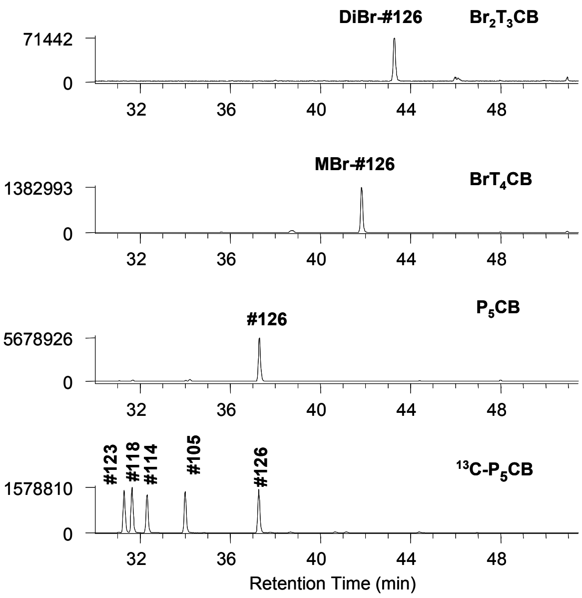


Figure 2 GC/MS chromatogram in contaminated $FeCl_3$
Co-PXB: #126 (PeCB, MBrTeCB, DiBrTrCB)

Figure 3 shows the results of fluorescent X-ray analysis on used etching liquid, liquid $FeCl_2$ and liquid $FeCl_3$. The used etching liquid was found to contain a high concentration of Cu and a trace of Br in addition to Fe and Cl. The major PCB congeners in the contaminated liquid $FeCl_3$ were 3,3',4,4',5-PeCB (#126), 3,3',4,4',5,5'-HxCB (#169). In the manufacturing process, metal iron is added to used etching liquid ($FeCl_2$ and $FeCl_3$) and recover Cu and Ni. The used etching liquid is then recycled by blowing chlorine into the reduced $FeCl_2$. In the past, the printed circuit boards contained brominated flame retardant (tetra-bromo-bisphenol-A, PBrDPE) and epoxides of Tetrabromobisphenol-A (glycidyl-ether of phenolic OH group) were used. The existence of brominated compounds is predicted such as epoxide of Tetrabromobisphenol-A in used etching liquid. Etching liquid contains $CuCl_2$ and brominated compounds, and has extremely low pH.

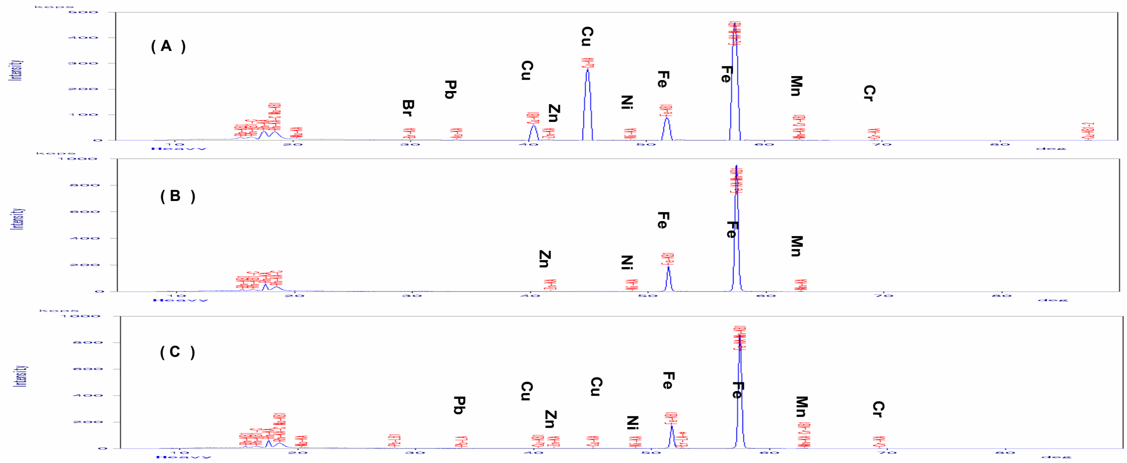


Figure 3 Fluorescent X-ray analysis of liquid samples (A) used etching waste, (B) $FeCl_2$, (C) $FeCl_3$

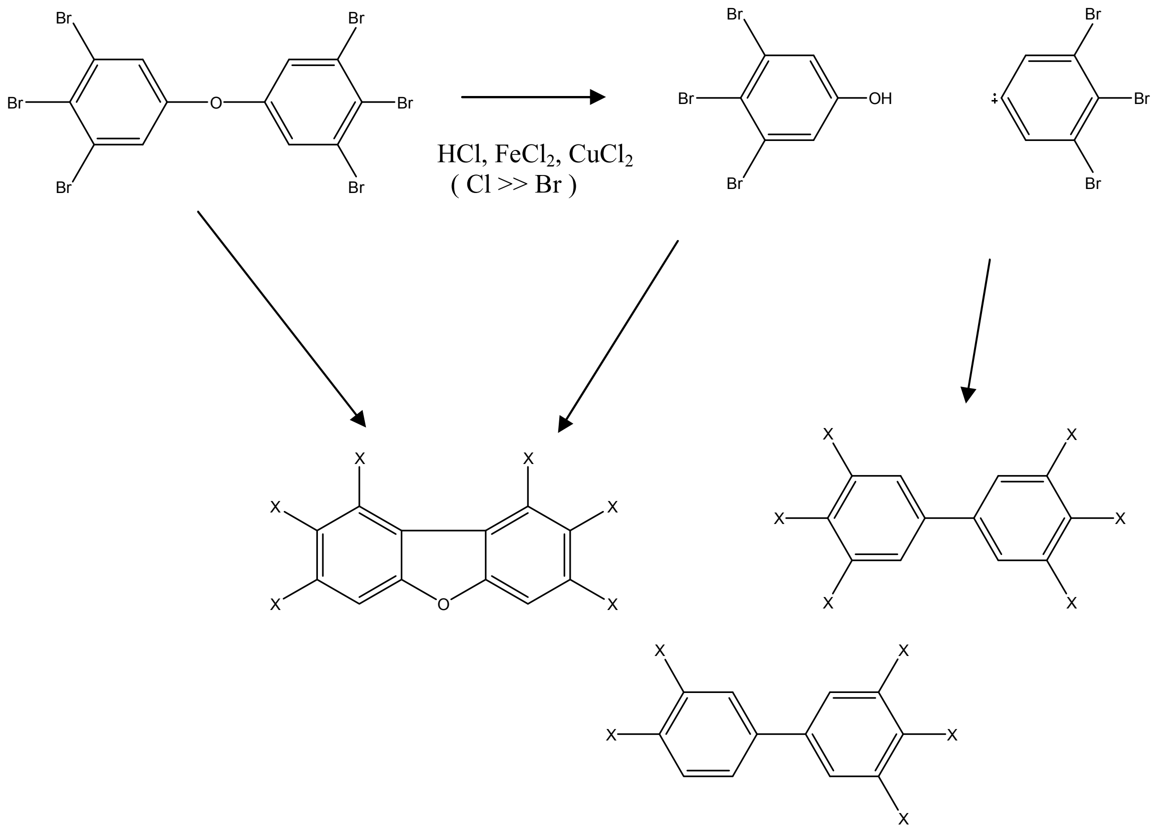


Figure 4 PBrDPE in strongly acidic solution in presence of HCl, $FeCl_2$ and $CuCl_2$.

Grabda et al. present theoretical calculations of thermodynamic properties of BFRs using Density Functional Theory methods. For PBDEs and polybrominated biphenyls, the Gibbs free energy of formation increases with additional bromines. Br substitution at the ortho position is energetically unfavourable compared to meta and para substitution[1]. PBrDPE might be decomposed to polybromophenol and polybromobenzene radical in strongly acidic solution in the presence of HCl, $FeCl_2$ and $CuCl_2$. Dimerization of polybromobenzene radical forms Co-PXB with selective debromination and Br-Cl substitution. The contaminated $FeCl_3$ contained halogenated (bromo-chloro) biphenyl with mixed Br and Cl, though its concentration was lower than chlorinated biphenyl (PCB-126). It is expected that the PCB-126 precursors exist in liquid $FeCl_2$, which mainly form PCB-126. It is essential to integrate the system for PCB removal into the manufacturing process in order to reduce PCB concentration in liquid $FeCl_3$.

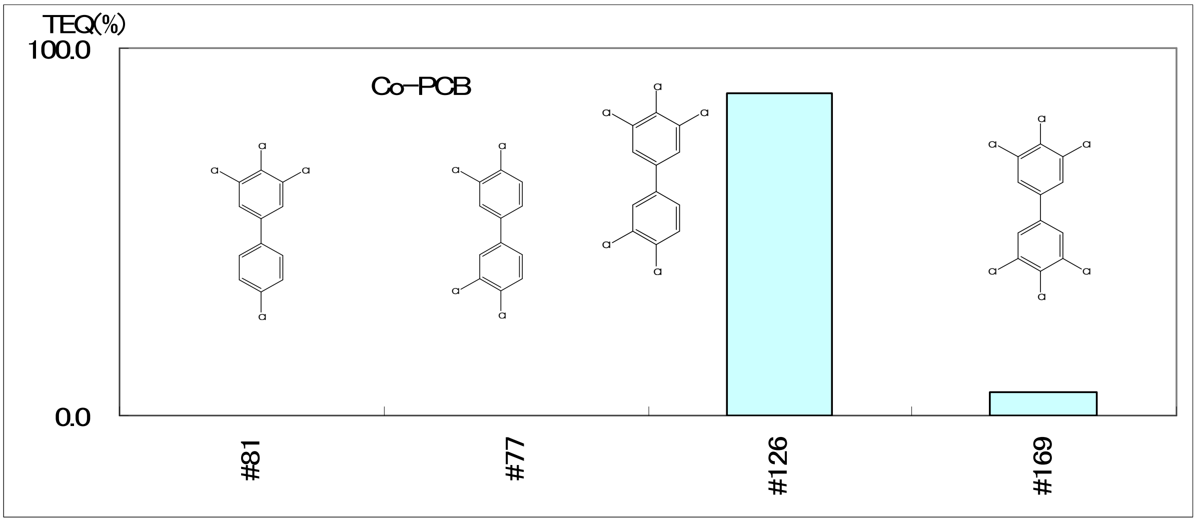
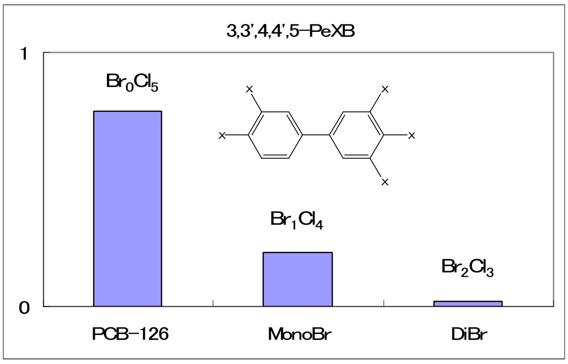


Figure 5 TEQ contributions (%) of co-PCB in $FeCl_3$



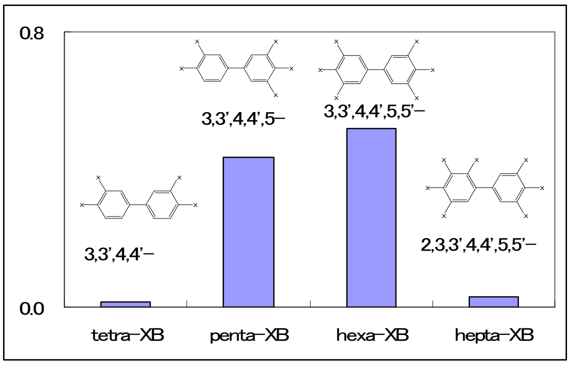


Figure 6 Distributions of 3, 3, 4, 4, 5-PeXB in $FeCl_3$.

Figure 7 tetra-, penta-, hexa-, and hepta-XB. in $FeCl_3$

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References

1. Grabda M, Oleszek-Kudlak S, Shibata E, Nakamura T, *Organohalogen Comp* 2006; 68:1983.