# FORMATION OF DIOXINS FROM OPEN BURNING OF CABLE: EFFECT OF COPPER AND INVESTIGATION OF THE MECHANISMS

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## Introduction

End-of-Life management of waste electrical and electronic equipment (WEEE) is causing great concern, since primitive, poorly controlled recycling techniques, particularly in developing countries, are generating excessive environmental pollution<sup>1</sup>. It is still common practice in many parts of the world to use open burning to recover metal values (mainly copper) from plastics, in which they are encased, during WEEE recycling operations. Polyvinylchloride (PVC) is a prevailing insulation material in electrical and electronic equipment due to its low price, high flame resistance and excellent electrical insulation. In open burning of WEEE (especially cables), all ingredients to form dioxins are abundantly present: carbon and chlorine (PVC), and a catalyst (copper)<sup>2</sup>. Gullett et al.<sup>3</sup> simulated practices associated with rudimentary metal recovery operations of cables and circuit boards and the average emission factors of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) were 11,900 and 92 ng TEQ/kg, respectively. These exceptionally high PCDD/F emissions from cable burning were exacerbated by the high concentration of PVC-based insulation (65 wt.%) combined with the presence of copper (35 wt.%). A field survey at an open burning site of WEEE reported a significant positive correlation between concentrations of copper and PCDD/F<sup>4</sup>. Though known as a serious emission source<sup>5</sup> and having led to desperately high concentrations of PCDD/F in local environment<sup>6, 7</sup>, open burning of WEEE has seldom been studied for its reaction mechnisms of forming PCDD/F.

In this study, a mixture of PVC and metallic copper simulating cables coated with PVC and a pure PVC sample are compared for their thermogravimetric behaviors during combustion, species of chlorine after being heated at different temperatures and outputs and signatures of PCDD/F. The primary aim is to study the exact effect of copper on forming dioxins during cable burning. The analyses of resulting data offer essential information for investigating the reaction mechanisms of dioxins formation from the viewpoints of both reactants (thermogravimetry and changes in chlorine) and products (PCDD/F signatures).

## Materials and methods

**Thermogravimetric analysis.** Thermogravimetric behaviors of powdery PVC resin and the mixture of PVC and copper powder in weight ratio of 5:1 (denoted as 'PVC + Cu') were studied by TG–DTA in a flow of synthetic air (20.7%  $O_2 + N_2$ , 50 mL/min). Temperature was raised from room temperature to 800 °C at a heating rate of 5 °C/min. The thermogravimetric weight loss curve (TG, %) and the derivative curve of the weight loss (DTG, %/min) were plotted as a function of temperature.

**Cl K-edge XANES.** PVC and PVC + Cu were mixed with boron nitride (BN), respectively, producing two mixtures containing the same PVC content (16.7 wt.%). The mixtures were both heated for 30 min under synthetic air flow (50 ml/min) at three different temperatures (200, 300 and 400 °C, respectively). Then the Cl K-edge X-ray Absorption Near Edge Structure (XANES) spectra of the heated mixtures were measured (at BL-11B in Photon Factory, Tsukuba, Japan) and analyzed for determining the forms of chlorine. Three categories of chlorine species were selected as Cl-references: (i) chlorine bonded with Cu (CuCl<sub>2</sub> and CuCl), (ii) chlorine connected to aromatic carbon (2,6-, 2,3,4,6-CP and PeCBz, Aromatic-Cl) and (iii) chlorine connected to aliphatic carbon (PVC, Aliphatic-Cl). Ratios of different Cl-species (%) in the heated samples were determined by linear combination fitting (LCF) using the reference materials (fitting range: 2814 to 2824 eV).

**PCDD/F formation tests.** The PCDD/F-formation tests were conducted in a vertical tubular reactor surrounded by an electric furnace and operating substantially at atmospheric pressure<sup>8</sup>. A sample of 2 g of PVC or PVC + Cu was placed into a vertical quartz tube, which was then introduced into a preheated electric furnace for 60 min at three different temperatures (200, 300 and 400 °C, respectively), in a synthetic air stream supplied at 50 ml/min. After heating, the PCDD/F remaining in the quartz tube (including the char residue and all substances adhering on the inside wall of the quartz tube, regarded as solid-phase sample) and those in the gas phase and collected by XAD-2 and the toluene impinger (treated as gas-phase sample) were analyzed separately.

## **Results and discussion**

**Effect of Cu during combustion of cable.** Figure 1 presents the TG-DTG results of PVC and PVC + Cu heated in synthetic air at 5 °C/min. As seen, thermal degradation of pure PVC in air takes place in three steps: (I) dehydrochlorination (200-350 °C, weight loss: 63%), release of HCl, followed by cyclization reactions forming aromatic and alkyl aromatic species; (II) condensation (350-420 °C, weight loss: 3%), progressive formation of

poly-condensed aromatic intermediates; (III) fragmentation (> 420°C, weight loss: 33%), oxidative destruction of the poly-condensed aromatic intermediates and release of hydrocarbons<sup>9</sup>. The addition of Cu merges the three-step degradation of PVC into two steps (240-300 °C, weight loss: 44%; 300-550 °C, weight loss: 36%), by incorporating condensation and fragmentation to a continuous stage. The last 20 wt.% residue is CuO (theoretical value: 20.8 wt.%). Overall, the presence of Cu during combustion of cable suppresses the volatilization of Cl from solid at lower temperature, reduces the temperature required for formation of poly-condensed aromatic intermediates, and largely promotes the decomposition of the poly-condensed carbon-matrix by its oxide at higher temperature.



Figure 1. Thermogravimetric results of PVC and PVC + Cu heated in synthetic air at 5 °C/min.



Figure 2. Cl K-edge XANES spectra of PVC (a) and PVC + Cu (b) heated in synthetic air at different temperatures and the reference standards.

**Influence of Cu on chemical forms of Cl.** Figure 2 shows the XANES spectra of Cl in PVC and PVC + Cu (mixed with BN) heated in synthetic air at three different temperatures. Before heating, all Cl is in form of PVC (Aliphatic-Cl), with the absorption peak locating at 2820.6 eV. No obvious changes in the spectra are observed in both samples after heating at 200 °C. After being heated at 300 °C, the Cl-XANES spectra show obvious distinctions: the peak position of Cl-XANES spectrum in PVC moves almost invisibly, while the shape changes notably; the absorption peak of Cl-XANES spectrum in PVC + Cu shifts to 2821.3 eV, rightly dropping into the range of Cl connected to aromatic carbon (2821.1-2821.3 eV), and the shape presents as a combination of the three

types of reference standards. After heating at 400 °C, the Cl-XANES peak in PVC shifts to 2820.8 eV, still lower than the positions of Aliphatic-Cl; the Cl-XANES spectrum in PVC + Cu presents its shape similar to those of CuCl and CuCl<sub>2</sub>. Ratios of different Cl-species (%) in the heated samples estimated by LCF are shown in Figure 3. In PVC, the Cl in solid residue is partially transformed to Aromatic-Cl, as a result of cyclization and condensation reactions of the carbon skeletons, and the ratio of Aromatic-Cl grows with higher temperature. While the LCF results of PVC + Cu are different, especially for those at 300 and 400 °C: at 300 °C, most Cl in solid residue is transformed to other species, with the ratios of Cl-species in a decreasing order of CuCl > Aromatic-Cl = Aliphatic-Cl; at 400 °C, organic-Cl species are mostly released from solid residue, resulting in the remaining Cl mainly in form of inorganic Cu-Cl species. The comparison suggests that the presence of Cu in combustion of cable accelerates the cyclization, condensation and oxidation of the carbon skeletons, as a result, promoting the transformation of the Cl in PVC (in solid residue) into other species.



Figure 3. The percentage of Cl-species in heated samples estimated by LCF.

**Output of PCDD/F.** Figure 4 shows the PCDD/F output (in ng/g-PVC) from PVC and PVC + Cu heated at different temperatures and the distribution between the solid-phase and gas-phase sample. For both PVC and PVC + Cu systems, the yields of PCDD/F increase with the rising temperature from 200 to 400 °C. At 200 °C, PCDD/F outputs from PVC and PVC + Cu are marginal and comparable (9.3 and 7.2 ng/g-PVC, respectively). At higher temperatures, the rise of PCDD/F yield from PVC + Cu attains a factor of 6.5 (at 300 °C) and 8.9 (at 400 °C) compared with that from pure PVC, confirming the promoting effect of Cu on formation of dioxins from cable burning. The trend of PCDD/F toxic equivalence quantity (TEQ) influenced by Cu and varying with temperature is similar to that of PCDD/F output (Table 1). For the PVC system, the amount of PCDD/F remaining in solid-phase increases with higher temperature (Figure 4), consistent with the gradually rising tendency of Aromatic-Cl ratio in the solid residue (Figure 3). For the PVC + Cu system, however, the trend of PCDD/F in solid-phase (Figure 4) is different from that of Aromatic-Cl ratio in solid residue (Figure 3), especially for the case at 400 °C. One explanation for this discrepancy is that the large amount of soot and tar depositing on the inside wall of the quartz tube produced from PVC + Cu at 400 °C are also included in the solid-phase sample for PCDD/F analysis, together with the char residue; while the Cl-XANES technique can only reflect the chemical forms of Cl remaining in the char residue.



Figure 4. PCDD/F output (ng/g-PVC) as a function of temperature.

**Analysis of PCDD/F signatures.** Formation of PCDF is favored over that of PCDD, except for PVC heated at 300 °C (Table 1). A tendency of increasing ratio-PCDF/PCDD with higher temperature is observed in the PVC + Cu system, constant with that noticed by Shibata et al.<sup>10</sup> in PVC pyrolysis with CuO. The weight-averaged chlorination levels of PCDD, PCDF and PCDD/F in both systems achieve their minimum values all at 300 °C (Table 1), suggesting 300 °C as a pivotal point for the formation pathways of PCDD/F. This is also indicated by their homologue distribution patterns (not shown). Isomer-specific information is essential for analyzing PCDD/F

formation mechanisms. Figure 5 represents the PCDD-isomer signatures for PVC and PVC + Cu samples tested at different temperatures. The distribution patterns of PVC + Cu at 300 and 400 °C are distinct from that of the other four samples, especially at 1,3,6,8- and 1,3,7,9-TCDD, and x,x,x,6,8- and x,x,x,7,9-PeCDD, indicating differences existing in the formation pathways. Earlier study<sup>11</sup> suggests the existence of a distinctive PCDD-congener pattern, associated with the condensation of the released precursors (especially CP) and comprising the six PCDD-congeners mentioned above, as well as 1,2,3,4,6,8-HxCDD. Figure 5 shows that rising temperature and adding Cu turn the PCDD-pattern from dominated by the CP-route congeners to composed of all congeners in more equal amount. It suggests that the oxidative destruction of carbon-matrix and direct release of PCDD/F are promoted.

Table 1.	TEQ, ratio	of PCDF to	PCDD and	l chlorination	level of	f different samples.
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Figure 5. Isomer distributions (%) of PCDD as a function of temperature.

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