Real-Time Gas-Phase Analysis of Mono- to Tri-Chlorobenzenes Generated from Heated MSWI Fly Ashes Containing Various Metal Compounds: Application of VUV-SPI-IT-TOFMS

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We measured sensitive real-time change of low-chlorinated (Cl₁−Cl₃) benzenes in gas phase from heated model and real solid samples using the recently developed vacuum ultraviolet (VUV) single-photon ionization (SPI) ion trap time-of-flight mass spectrometer (VUV-SPI-IT-TOFMS). Model solid samples that contained activated carbon, potassium chloride, silicon dioxide, and trace metallic compounds (copper, iron, lead, and zinc) were used to simulate fly ash at a municipal solid waste incinerator (MSWI). The concentrations of chlorobenzenes determined by integrating the area for chlorobenzenes was developed. Various types of real-time measurement techniques are expected to have novel applications for the study of time-dependent formation of gas-phase chlorinated organic compounds (9–11).

Chlorinated aromatic compounds such as dioxins and chlorobenzenes are known to be emitted from anthropogenic thermal processes. Homo- and heterogeneous formations of chlorinated aromatic compounds from macromolecular carbons have been suggested in many studies (12–14). Fly ash collected from the postcombustion zone in MSWIs has the highest potential for forming chlorinated aromatic compounds (12, 13). Recently, the authors reported that metal species and their chlorides and oxides strongly affect the formation path of chlorinated aromatic compounds in the solid phase of fly ash (15). Thus, gas-phase real-time formations of low-chlorinated benzenes are implied to also depend on metallic forms, which provide instantaneous time scale knowledge about VOCs such as low-chlorinated benzenes based on the presence of particular metallic compounds. However, typically, the fine time scale measurement of chlorinated organic compounds has been difficult because conventional gas chromatography/mass spectrometry (GC/MS) analysis required too much time to measure and analyze the compounds under a single experimental condition.

Here, we report the availability of sensitive real-time gas-phase measurement to estimate the formation mechanism of low-chlorinated benzenes during the heating of real and model fly ash mixed with various metal species using the recently developed vacuum ultraviolet (VUV) single-photon ionization (SPI) ion trap time-of-flight mass spectrometer (VUV-SPI-IT-TOFMS) (7). Comparing four species of metal (copper, iron, lead, and zinc) and their oxides, chlorides, and other forms, we show that metallic compounds identify the real-time formation of low-chlorinated benzenes from model fly ash under the same experimental conditions. Real-time change pattern features of many types of samples mixed with metal species suggest the main factor for the generation of gas-phase chlorobenzenes and other chlorinated organic compounds, such as dioxins scattered from real fly ash in MSWIs.

Materials and Methods
Real and Model Fly Ash. Real fly ashes were collected from a bag filter (BF) and electrostatic precipitator (ESP) at a MSWI. Any organic compounds in activated carbon (Takeda Phar-
maceutical Co., Ltd., Osaka, Japan) were removed by heating at 500 °C for 60 min under a 100% nitrogen gas stream (100 mL/min), and removed activated carbon was referred to as “AC” in this report. The AC contained few metal species. To determine the effect of metal species, model fly ashes were prepared and mixed by grinding the following in a mortar for about 10 min: AC (3.0 wt %), potassium chloride (KCl; 10 wt % Cl), metal compounds (0.2 wt % metal), and silicon dioxide (SiO₂; remainder). Note that model fly ash without metal compounds, a mixture of AC+KCl+SiO₂, was called a “blank” in the previous report. Metal species included CuCl₂·2H₂O (purity 97%), Cu₂(OH)₃Cl known as atacamite (high purity; Nichika Corp., Kyoto, Japan), CuCl (95%), CuO (97.3%), Cu₂O (99.5%), Cu(OH)₂ (>95%), Cu₂O·Cu(OH)₂·2H₂O (55% as Cu), FeCl₃ (97%), FeCl₂·6H₂O (99%), FeCl₃·4H₂O (>99%), Fe₂O₃ (95%), PbCl₂ (99%), PbO (99%), ZnCl₂ (98%), and ZnO (99%).

Low-Chlorinated Benzenes Monitored by VUV-SPI-IT-TOFMS. A 5.0 g portion of real or model fly ash was inserted on a quartz boat into a quartz tube (120 cm × 4 cm i.d.) filled with 10% oxygen (90% nitrogen) gas at 50 mL/min and heated for 30 min in an electronic furnace preheated to 300 °C. Connected to VUV-SPI-IT-TOFMS at the outlet of the quartz tube, we measured real-time changes in low-chlorinated benzenes in the outlet gas, as illustrated in Figure S1 in the Supporting Information (SI). Low-chlorinated benzenes in gas phase were ionized by a single photon of vacuum ultraviolet, Lyman α light (wavelength, 121.6 nm; photon energy, 10.2 eV), and the target ions were trapped and ionized in the ion trap, and detected by a time-of-flight mass spectrometer. The VUV light (10¹⁴ photons cm⁻² s⁻¹) is introduced through a MgF₂ window into the ion trap in the vacuum chamber. The ionization efficiency by VUV-SPI-IT-TOFMS did not decrease, as reported previously in detail (6). As the ionization intensity is maintained by integration, highly sensitive real-time measurements can be made. Achieved one-measurement time was ca. 18.3 s. By controlling the temperature at 300 °C and inserting the quartz boat as quickly as possible, we monitored mono-, di-, and trichlorobenzenes, called M1CBz (monochlorobenzene), D2CBz (1,4-dichlorobenzene), and T3CBz (1,2,4-trichlorobenzene), per 20 s in the outlet gas from the connection at 50 mL/min (see Figure S2b). The lower detection limit was determined to be ca. 10 ppt level of T3CBz. In the following figures, the dashed and bold lines indicate data per 20 s and the moving average data of 11 points (i.e., 0, ±20, ±40, ±60, ±80, ±100 s each time). Toluene in an impinger trapped organics in the outlet gas (also 50 mL/min) and was also analyzed by GC/MS for D2 and T3CBz. The GC/MS analysis procedure has been reported elsewhere (15).

Results and Discussion

Formation of Gas-Phase Low-Chlorinated Benzenes from Heated Real Fly Ashes. We succeeded at monitoring the high-resolution real-time change of CBzs in gas phase. When two real fly ashes were heated at 300 °C for 30 min in an electric furnace, low-chlorinated benzenes generated in gas phase (Figure 1). Two-type raw fly ashes contained 10 ng/g levels of D2 and T3CBz, respectively. Reheating fly ashes generated two or more order higher contents of D2 and T3CBz. Although volatilization of remaining low-chlorinated benzenes was partly thought to influence real-time measurement, we assessed its effect as negligible. As the concentration of M1CBz had a higher baseline than that of D2 and T3CBz, its precise concentration was determined by deduction of the baseline as explained in Figure S2a.

Focusing attention on the position and height of the first peak defined as the time (min) and height (ppb) of the first appearance of peaks in the real-time pattern, the first peak positions of M1, D2, and T3CBz were 4.0, 14.2, and 15.0 min (captured by BF), and 12.8, 15.8, and 16.2 min (ESP), respectively; first peak heights showed 1300, 370, and 360 ppb (BF), and 2300, 230, and 110 ppb (ESP), respectively (Table 1). Then, we needed to specify causative elements to generate gas-phase low-chlorinated benzenes from the heated solid phase of real fly ash. However, real fly ash contains numerous elements. As chlorinated benzenes have chlorine in their chemical structure, a chlorine source in real fly ash is thought to be important to assess the promoting factor in gas-phase formation of low-chlorinated benzenes. Inorganic chlorines, such as KCl and NaCl, were the main chemical forms of chlorine in real fly ash reported by Zhu et al. (16). So, we prepared a simple model fly ash, calling it the blank, containing KCl as the chlorine source, a carbon source (AC), and SiO₂ matrix. Although the first peak height of the blank was detected as 200 ppb at 6.0 min in M1CBz, D2 and T3CBz were not detected (Figure 2a and Table 1).

| TABLE 1 | Various First Peak Positions and First Peak Heights of Real-Time Change Patterns of Model and Real Fly Ashes* |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| metal compounds | M1CBz | D2CBz | T3CBz |
| A. oxide-like compounds of copper |
| CuO | 11.0 | 14.8 | 16.0 | 400 | 620 | 520 |
| Cu₂O | 13.1 | 14.5 | 15.9 | 410 | 550 | 390 |
| Cu(OH)₂ | 15.5 | 14.0 | 15.3 | 340 | 230 | 250 |
| Cu₂O·Cu(OH)₂·2H₂O | 10.0 | 12.9 | 14.3 | 320 | 580 | 550 |
| B. chloride-like compounds of copper |
| CuCl₂·2H₂O | 10.8 | 20.0 | 22.5 | 5500 | 1200 | 850 |
| CuCl(OH)₂Cl | 11.8 | 11.6 | 14.0 | 3300 | 3000 | 2000 |
| CuCl | 13.2 | 19.1 | 22.0 | 1200 | 700 | 350 |
| C. chlorides of iron |
| FeCl₃ | 11.0 | 12.5 | 13.5 | 6300 | 1300 | 230 |
| FeCl₃·6H₂O | 11.2 | 12.1 | 13.1 | 4500 | 510 | 320 |
| FeCl₃·4H₂O | 11.8 | 12.5 | 14.8 | 6100 | 430 | 30 |
| D. blank-like compounds |
| PbO | 10.0 | n.d. | n.d. | 90 | n.d. | n.d. |
| PbCl₂ | 12.5 | n.d. | n.d. | 120 | n.d. | n.d. |
| real fly ashes |
| fly ash (BF) | 4.0 | 14.2 | 15.0 | 1300 | 370 | 360 |
| fly ash (ESP) | 12.8 | 15.8 | 16.2 | 2300 | 230 | 110 |

* These two values clearly divided the real-time change patterns into four group types: (A) oxide-like compounds of copper, (B) chloride-like compounds of copper, (C) chlorides of iron, and (D) blank-like compounds. n.d. = not detected.
The influence of KCl on the formation of gas-phase low-chlorinated benzenes was much less than that of real fly ashes. As for the formation of solid-phase chlorinated aromatics, inorganic chloride also showed little influence (15, 17, 18). To estimate the effective element, we should study other chlorine sources or catalysts such as trace metal compounds in real fly ash.

**Metal Species Specify the Real-Time Change Patterns of Exhausted Chlorobenzenes.** Model fly ashes containing various metal compounds consisting of Cu, Fe, Pb, and Zn showed characteristic gas-phase real-time change patterns during heating at 300 °C for 30 min (Figures 2 and 3, Table 1). Some metal compounds had a stronger influence than real fly ashes on the formation of chlorinated benzenes in gas phase. Hence, some trace metal compounds in real fly ash were concluded to be the causative elements to promote gas-phase low-chlorinated benzenes. In this section, we discuss the real-time change patterns characterized by metal compounds.

The metal compounds could be divided clearly into four major groups by comparing the shapes of the real-time change patterns: (A) oxide-like compounds of copper, (B) chloride-like compounds of copper, (C) chlorides of iron, and (D) blank-like compounds. First, however, we verified the accuracy of the real-time VUV-SPI-IT-TOFMS measurements by correlation with the concentrations of D2 and T3 benzenes in a toluene trap as analyzed by GC/MS. Calculating the area of real-time change excluding the baseline, we estimated the amounts of M1, D2, and T3CBz in gas phase for 30 min during the heating of each model fly ash (Figure S3). Figure S4 shows that the order of the area calculated indicated a positive correlation with the order of concentrations of D2 ($r = 0.79$) and T3CBz (0.83) as determined by GC/MS.

The group D blank-like compounds contained the blank (Figure 2a), ferric, lead, and zinc oxides (Fe$_2$O$_3$, PbO, and ZnO; Figure 2f, g, and h, respectively), and lead and zinc chlorides (PbCl$_2$ and ZnCl$_2$; Figure 3g and h, respectively). The first peak heights of M1CBz were the smallest and between 90 and 200 ppb appeared at 6.0–12.5 min (Table 1). For D2 and T3CBz, the first peak heights were not detected by VUV-SPI-IT-TOFMS because the detection limit was thought to be less than 10 ppb in the present study. When model fly ash with added zinc chloride (ZnCl$_2$) and one of the blank-like compounds was heated at 300 °C for an expanded 120 min, gas-phase low-chlorinated benzenes were hardly detected, except for a little formation of M1CBz until around 20 min (Figure 4c). Blank-like compounds had little effect on gas-phase formation of low-chlorinated benzenes during heating. So, we estimated these compounds in real fly ash to have little impact on the generation of gas-phase low-chlorinated benzenes.

Causative metal compounds associated with the generation of low-chlorinated benzenes in gas phase were considered to belong to three groups: A, B, and C. Copper forms bonded to an oxygen atom, not to chlorine (oxide-like compounds of copper, (B) chloride-like compounds of copper, (C) chlorides of iron, and (D) blank-like compounds. First, however, we confirmed the accuracy of the real-time VUV-SPI-IT-TOFMS measurements by correlation with the concentrations of D2 and T3 benzenes in a toluene trap as analyzed by GC/MS. Calculating the area of real-time change excluding the baseline, we estimated the amounts of M1, D2, and T3CBz in gas phase for 30 min during the heating of each model fly ash (Figure S3). Figure S4 shows that the order of the area calculated
M1, D2, and T3CBz showed the same level at 320–410, 230–620, and 250–550 ppb, respectively (Table 1). Therefore, low-chlorinated benzenes were distributed in the sequence M1 (12.4 min) → D2 (14.1 min) → T3CBz (15.4 min), at the same level at 430 (standard deviation) ppb (n = 12) in the case of mixtures of the group A oxide-like compounds (Figure 5a). Although the chlorine source was only KCl in the model fly ash of group A, the amounts of chlorobenzenes in group A were higher than those of the group D, blank-like compounds (Table 1 and Figure S3). This is because gas-phase low-chlorinated benzenes were thought to be catalyzed by copper oxide, and oxide-like forms catalyzed via Deacon-like reaction (19, 20) using KCl as a chlorine source in solid phase.

Copper compounds connected to chlorine, called chloride-like compounds of copper (group B in this paper) such as cupric chloride dihydrate (CuCl₂·2H₂O), atacamite (Cu₂(OH)₃Cl), and cuprous chloride (CuCl), showed characteristic real-time change patterns and strongly affected the gas-phase formation of low-chlorinated benzenes. Chlorobenzenes in gas phase changed with first maximum peaks at around 11.9 (M1CBz), 16.9 (D2), and 19.5 (T3) min and ordered M1 (3300 ppb, mean) > D2 (1600 ppb) > T3CBz (1100 ppb) during heating for 30 min (Table 1 and Figure 3a–c). Figure 5b shows the features of first peak positions and heights of chloride-like compounds of copper (b–e, as shown in Figure 2) was not measured for the 120-min span.

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during heating for 30 min. These results implied that the second gas-phase real-time formation pattern over 30 min, \( T_3 > D_2 > M_1 \text{CBz} \) (Figure 4a), was caused by the thermal destruction of carbon.

Chlorides of iron have been reported to be effective promoters of the formation of chlorinated aromatic compounds in solid phase such as fly ash (15, 23). In gas phase, chlorides of iron also had a strong effect on the generation of chlorinated aromatics from the real-time measurements using VUV-SPI-IT-TOFMS. Without the valence of Fe(II) or Fe(III), chlorides of iron (ferric chloride, FeCl₃; ferric chloride hexahydrate, FeCl₃·6H₂O; and ferrous chloride tetra-hydrate, FeCl₂·4H₂O) in group C promoted the same level of low-chlorinated benzenes (Figure S3) and exhibited an original pattern of real-time change, as shown in Figure 3d, e, and f, respectively. The first peak positions of M₁, D₂, and T₃CBz occurred at about 11.3, 12.4, and 13.8 min, respectively. Specifically, these were distinguished from other metal compounds in that more lower chlorinated benzenes were generated in gas phase during heating, i.e., M₁ (5600 ppb, first peak height) \( \gg \) D₂ (680 ppb) \( \gg \) T₃CBz (93 ppb) (Table 1, Figures S3 and 5c). Heating for 120 min, the real-time amounts of low-chlorinated benzenes, M₁, D₂, and T₃CBz, remained stable at around 4000, 300, and 100 ppb, respectively, over 30 min (Figure 4b). According to these results, the lower chlorinated benzene in gas phase was preferentially promoted by iron chlorides. Promotion of chlorinated aromatic compounds in fly ash (solid phase) by oxychlorination of iron chloride (24) is thought to cause the formation of low-chlorinated benzenes in gas phase.

Effect of Metal Species in Real Fly Ash Analyzed by Real-Time Features. According to the real-time changes of M₁, D₂, and T₃CBz in the model system categorized into four groups, we attempted to infer the contribution to the gas-phase formation of low-chlorinated benzenes from heated real fly ashes. We plotted first peak positions and heights from groups A through D in a two-dimensional plane (Figure 6) to identify the metal compounds causing the formation of gas-phase low-chlorinated benzenes from heated real fly ashes collected by BF and ESP (Figure 1). If a plot of a real fly ash was included in the area composed of each group, low-chlorinated benzenes in gas phase were estimated to be influenced mainly by the metal compounds in each group. Figure 6a shows that the plot of M₁CBz from real fly ash collected by ESP was included in group B. The first peak height of M₁CBz from real fly ash collected by BF had the same level of chloride-like compounds of copper, although real fly ash (BF) showed the most rapid first peak position, 4.0 min, in all samples (Table 1). More real-time patterns of real and model fly ashes were needed by VUV-SPI-IT-TOFMS to reveal the correct factors. Yet, trace chloride-like compounds of copper in real fly ash were implied to affect mainly the formation of gas-phase M₁CBz. The area of group A for D₂ and T₃CBz (Figure 6b and 6c, respectively) contained the plot of real fly ash collected by BF and located the nearest plot of real fly ash collected by ESP. So, oxide-like compounds of copper (group A) in real fly ash were thought to be the main causative metallic compounds in the catalytic formation of D₂ and T₃CBz in gas phase. The amount of copper (0.20–0.26 wt %) was less than that of Fe (0.47–1.0 wt %), Pb (0.52–0.75 wt %), and Zn (1.4–1.7 wt %) in these real fly ashes, which we have measured before (25). However, the relatively trace copper compounds (e.g., oxides, chlorides) in a real fly ash seemed to make the most powerful contribution to the gas-phase formation of low-chlorinated benzenes. The influences of lead and zinc compounds (oxides and chlorides) in real fly ash on the formation of gas-phase low-chlorinated benzenes were thought to be rather weak in terms of the real-time measurement of model fly ashes (Table 1). Although iron chlorides showed strong contributions to the formation of gas-phase low-chlorinated benzenes, iron oxide had a weak contribution. The main chemical form of iron in real fly ash has been summarized as oxides (Fe₂O₃ and FeO) by Kirby and Rimstidt (26). Thus, we suggest that iron compounds in real fly ash did not have a great influence on the generation of gas-phase low-chlorinated benzenes. Nonetheless, some part of the chemical form of iron in real fly ash may exist in a chloride form to strongly promote gas-phase low-chlorinated benzenes in gas phase.
chlorinated benzenes. These results using real-time features such as the first peak position and height indicate the importance of trace metal compounds, especially chloride- and oxide-like compounds of copper, in real fly ash on the generation of gas-phase low-chlorinated benzenes.

Our novel research using VUV-SPI-IT-TOFMS provides useful and original knowledge to characterize the gas-phase formation of low-chlorinated benzenes. We concluded that real-time sensitive measurements of M1, D2, and T3CBz offer not only real-time features, but also the identification of causative factors by comparing model and real samples. The thermal process is thought to be a major anthropogenic source of gas-phase low-chlorinated benzenes. Thus, the monitoring and characterization of thermal processes by VUV-SPI-IT-TOFMS may contribute more detailed scientific information to protect the environment from pollution by low-chlorinated benzenes.

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Supporting Information Available
Four supporting figures. This information is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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