Unexpected Aldehyde Generation in the Exhaust Gas at Waste Incineration Facilities

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Acid gases generated during the thermal treatment of waste are neutralized using devices, such as bag filters coated with slaked lime. However, residual trace organic substances can react with the highly reactive slaked lime. This study investigates the dynamics of organic substances generated in the bag filter when slaked lime is used in the exhaust gas treatment process. The mechanism of aldehyde generation was clarified using head space gas chromatography mass spectrometer (HS-GC/MS). Results indicated that methanol was converted to formaldehyde at a conversion ratio of 0.097% and ethanol was converted to acetaldehyde at a conversion ratio of 0.260%. In addition, when amines used as emulsifiers during slaked lime production persisted in the matrix, acetaldehyde formed at a maximum concentration of 121 mg/m3. The simulation method developed in this study can be used for the initial evaluation of aldehydes unexpectedly produced in an incineration treatment facility.

Keywords Headspace-GC/MS, aldehydes, highly reactive lime, industrial waste incineration treatment facility, atmospheric pollution

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However, unlike 1,4-dioxane formation, the mechanism behind the increased formation of aldehydes after neutralization was unclear. Kosaka et al. noted that formaldehyde is produced by chlorinating amines in the aqueous phase. Further, amine emulsifiers are used in the production of highly reactive slaked lime used in bag filters of waste incineration facilities. Therefore, active chemical species are exposed to multiple side reactions in the combustion exhaust gas. For example, hypochlorous acid is produced from chlorine gas and is present in substantial amounts in the combustion gas. Moreover, Sekine and Kitahara reported that when ethanol is applied to the surface of plaster in an indoor environment, it reacts with calcium hydroxide to generate acetaldehyde, which undergoes aldol condensation with crotonaldehyde. However, ethanol and methanol have not been reported to exist in the exhaust gas from waste incineration facilities, since their emissions are not regulated for low toxicity. Therefore, the detection of high concentrations of aldehydes in exhaust gas may be attributed to the reaction between the highly reactive slaked lime and alcohol. Aldehydes are unstable in the gas phase and labeled by the DNPH method or other similar methods, converted to a stable derivative, and perform methods such as UV detection high performance liquid chromatography. A common analysis method for aldehydes is to collect aldehydes in an air collection tube containing DNPH, derivatize the aldehydes with DNHP, and perform methods such as UV detection high performance liquid chromatography. However, a weakness of DNPH/HPLC analysis is that when sampling air, high relative humidity and low collection temperature are required to maintain the collection efficiency. Such a method is not suitable for the direct analysis of exhaust gas because the exhaust gas cannot be sampled to the collection tube at a high temperature of 170°C. Therefore, an experimental system, which separates and analyzes aldehydes at the time of generation, is required. In this study, the one-pot evaluation method was developed to be able to characterize slaked lime used on a bag filter. In a headspace vial using a headspace gas chromatography mass spectrometer (HS-GC/MS) (Fig. 1), the reactions and analysis conditions can be changed to easily reproduce to some extent reactions that may occur at the gas/solid interface in the bag filter, like the generation of aldehyde. And because the generated gas is confined in a sealed container, the sampling of gas will not be incorrect. Further, the generation behavior of aldehydes was investigated. The purpose of this study was to investigate the generation of aldehydes in bag filters coated with highly reactive slaked lime, in waste incinerators.

Experimental

Reagents and chemicals

Formaldehyde and acetaldehyde standards were prepared for HS-GC/MS analysis. A formaldehyde standard solution (1000 mg/L methanol solution), acquired from Wako Pure Chemical Industries Ltd., was used as the formaldehyde standard. The acetaldehyde standard was prepared by diluting extra-pure acetaldehyde (ca. 99.5%) manufactured by Wako Pure Chemical Industries Ltd. with infinity pure ethanol (99.5%). Butanol manufactured by Wako Pure Chemical Industries Ltd. with infinity pure ethanol (99.5%). Fluorobenzene was used as an internal standard substance and was prepared by diluting chemical-grade fluorobenzene (Wako Pure Chemical Industries Ltd.) with toluene for air pollutant measurements. The reagent calcium hydroxide, manufactured by Wako Pure Chemical Industries Ltd., was used as the standard slaked lime sample.

Sample preparations

In order to reappear the reaction between lime and alcohol in bag filters to affirm the generation of acetaldehyde and to quantify the formation of it, 0.1 g of calcium carbonate reagent was weighed as a blank sample in a vial, capped with a special crimp cap using a silicon septum with a polyimide (PI) seal (manufactured by Shimadzu Corporation), and 10 μL of a standard solution was added using a syringe pump. Formaldehyde standard solutions were prepared by diluting a formaldehyde methanol solution with methanol to prepare liquid series of 50, 100, 200, 500, and 1000 μg/mL. Acetaldehyde standard solutions were prepared by diluting an acetaldehyde reagent with ethanol to prepare solutions of 50, 100, 200, 500, 1000, 2000, 5000, and 10000 μg/mL. Additionally, 5 μL of the internal standard was added using a syringe pump. The formaldehyde methanol solution and acetaldehyde ethanol solution were not mixed and calibration curves were prepared separately. Furthermore, samples with only the aldehyde standard solution and internal standard substance (without the blank lime sample) were prepared to evaluate the influence of the matrix.

For experiments conducted to evaluate the type and amount of aldehydes produced by the reaction of alcohols with standard slaked lime, 0.1 g of the slaked lime sample was weighed and placed in a headspace vial. The vial was capped, which could be used at temperatures up to 300°C. Thereafter, 1 - 10 μg of methanol or ethanol was added. As an internal standard, 5 μg of a 1000 μg/mL fluorobenzene toluene solution was added. A blank lime sample was also prepared. Additionally, a standard slaked lime sample was used as a sample in which the organic matter does not remain on the surface.
In experiments conducted to investigate the type and concentration of aldehydes generated by reacting hydrochloric acid produced in the incinerator with amines remaining in highly reactive lime with a bag filter, 0.1 g of the slaked lime sample was weighed in a 20-mL vial, and 5, 10, 15, or 20 μL of concentrated hydrochloric acid was added, and capped with a dedicated crimp cap. Then, 3 μL of the amine (2-ethanolamine, diethylamine, or triethylamine) and 5 μL of the internal standard substance were added.

In experiments conducted to evaluate the aldehyde formed by the reaction of hydrochloric acid and hypochlorous acid with an amine, which did not use a slaked lime sample, was calculated. The concentration of substances other than aldehydes was evaluated as the relative value of the ion intensity of the main peak. The Wiley MS libraries and National Institute of Standards and Technology (NIST) MS search program 11 were used to identify the compounds detected. Substances exhibiting similarity of 90% or more were evaluated.

### Results and Discussion

#### Examination of analysis conditions

A calibration curve was prepared by using standard solutions with varying concentrations of formaldehyde and acetaldehyde, without the addition of a matrix, such as slaked lime. However, acetaldehyde and methanol could not be separated near the retention time under the current GC/MS analysis conditions. Additionally, formaldehyde was not commercially available, except in a methanol solution. Therefore, separate formaldehyde and acetaldehyde calibration curves were prepared. For the formaldehyde curve, formaldehyde methanol solutions with concentrations ranging from 50 - 1000 μg/mL were used. The solution was volatilized in a 20-mL vial. The concentration of the gas in the vial was in the range of 25 - 500 mg/m³. The specific ion intensity of the standard samples at m/z 29 was measured using HS-GC/MS and a calibration curve (atmosphere conversion concentration (mg/m³)) of good linearity was obtained (y = 1869.9x + 18767, R² = 0.9988). For the acetaldehyde curve, acetaldehyde ethanol solutions with concentrations ranging from 50 - 10000 μg/mL were used. Gas state concentrations of aldehydes in the vial ranged from 25 - 5000 mg/m³. The specific ion intensity of the standard samples at m/z 44 was measured and a good linearity calibration curve (atmosphere conversion concentration (mg/m³)) was obtained (y = 11966.4x + 10387.8, R² = 0.9989). Further, the influence of matrix coexistence on adsorption was examined. However, as slaked lime reacted with methanol and ethanol (used as a solvents) to generate formaldehyde and acetaldehyde, respectively, it was not possible to create a calibration curve using a slaked lime as a matrix. Therefore, a blank lime sample, which does not react with alcohol and had similar chemical properties, was used instead. A calibration curve was created in the same atmospheric conversion concentration range. A good linearity was obtained between the concentration and specific ion strength (formaldehyde m/z 29, y = 1452.8x + 8427, R² = 0.9996; acetaldehyde m/z 44, y = 10255.8x – 18525, R² = 0.9976). In addition, the respective relative standard deviation was 3.6 and 3.9% when 50 μg/mL formaldehyde and acetaldehyde standard samples were measured five times. Thus, the limit of quantification was determined to be 25 mg/m³. When blank lime samples were added, they were reduced to 78 and 86% for formaldehyde and acetaldehyde, respectively, compared to no matrix addition.

Further, the influence of the matrix on the decomposition and adsorption of aldehydes was assessed. The heat retention time at the headspace sampler was set for 5, 10, 20, and 30 min. The lowest and highest relative intensity value of acetaldehyde was obtained after heating for 5 and 20 min. When the heating time is set at 5 and 20 min, the relative strength of acetaldehyde added with the blank lime is 109 and 123% of the samples without matrix, respectively. Thus, the influence of the adsorption of aldehydes on the matrix was significant. It was assumed that the effects of thermal decomposition were small. The heat retention temperature was set at 170°C, because the temperature of the gas passing through the bag filter at the incineration treatment facility was 170°C.²⁰

#### Aldehydes generation from slaked lime following alcohol addition

The generation of aldehydes was investigated when alcohols (methanol, ethanol, and butanol) reacted at 170°C with standard slaked lime samples. Figures 2(a) - 2(c), respectively, depict the chromatograms of methanol, ethanol, and butanol addition.

| Table 1 Analytical conditions for the HS-GC/MS of formaldehyde, acetaldehyde and other compounds |
|-------------------------------------------------|-------------------------------------------------|
| Head space sampler section                      | Oven temp.                                      |
| Heat-retention time                              | 170°C (5 min)                                   |
| Sample line temperature                         | 35°C (5 min)                                    |
| Transfer line temperature                       | 5°C/min                                         |
| Injection mode                                  | 290°C (10 min)                                  |
| Injection mode                                  | He                                              |
| Gas pressure for pressurizing vial              | 1.15                                            |
| Sample injection time                           | 1:15                                            |
| GC/MS section                                   | 240°C                                           |
| Temp. program: Initial temp.                    | 70 eV                                           |
| Program rate                                    | 300°C                                           |
| Final temperature                               |                                                |
| Ion source temperature                          |                                                |
| Ionization method                               |                                                |
| Ionization potential                            |                                                |
| Interface temperature                           |                                                |

GCMS-QP2010 Ultra™ (manufactured by Shimadzu Corporation) was used for gas chromatography mass spectroscopy. HS-20 (manufactured by Shimadzu Corporation) was employed as the head-space sampler. All measurements were performed in the scan mode (m/z 25 - 200). Additionally, CP-Sil 5 CB for formaldehyde column, manufactured by Agilent J & W (length 60 m × 0.32 mm i.d. × 8.00 μm film thickness), was used for formaldehyde separation. Table 1 lists the details of the HS-GC/MS analysis conditions. The amount of formaldehyde and acetaldehyde generated by the slaked lime samples was calculated per unit weight by employing the calibration curve method and using the relative value of the internal standard substance. Moreover, the analysis sample, which did not use a slaked lime sample, was calculated.
Formaldehyde was generated from methanol, acetaldehyde was generated from ethanol, and butanal was generated from butanol. When ethanol was added to slaked lime, crotonaldehyde was formed by aldol condensation of acetaldehyde; the result was consistent with Sekine and Kitahara. The amount of aldehyde generated when 1 – 100 $\mu$L of the alcohol was added (39 – 3900 g/m$^3$; atmospheric conversion concentration) and the rate of conversion of alcohols to aldehydes are shown in Fig. 3. An increase in the concentration of formaldehyde was also confirmed with methanol and ethanol at concentrations of 790 g/m$^3$ or more. The rate of conversion to aldehydes was calculated using a relationship between alcohols and aldehydes in the range of 0 – 316 g/m$^3$ as a line passing through the origin; it was 0.097% for formaldehyde and 0.260% for acetaldehyde. The conversion rate was calculated as:

$$\text{Conversion rate (\%)} = \frac{C_{\text{aldehyde}} \times V_{\text{vial}} \times M_{\text{alcohol}}}{\rho_{\text{alcohol}} \times V_{\text{alcohol}}} \times 100, \quad (1)$$

where $C_{\text{aldehyde}}$ represents the concentration of formaldehyde and acetaldehyde in air in vial, $V_{\text{alcohol}}$ represents the volume, $M_{\text{alcohol}}$ is the molar mass, $\rho_{\text{alcohol}}$ is the density of the added alcohol, and $V_{\text{vial}}$ is the HS vial volume, which was 20 mL.

Oguchi reported that formaldehyde and acetaldehyde were detected in concentration ranges of 0 – 290 $\mu$g/m$^3$ (0 $\mu$g/m$^3$ means not detected) and 2 – 1400 $\mu$g/m$^3$, respectively, in the final exhaust gas of waste incineration treatment facilities. It is assumed that formaldehyde and acetaldehyde were all produced by the reaction of slaked lime and alcohol, which Oguchi measured in the final exhaust gas. Substituting the concentrations of formaldehyde and acetaldehyde in the exhaust gas into formula (1) can be used to calculate the concentration of alcohol used in the reaction. Then, the concentrations of methanol and ethanol were calculated as 0 – 299 and 0.8 – 538 $\mu$g/m$^3$, respectively. In addition, since the thermodynamic stability of butanal is higher than formaldehyde and acetaldehyde, it is difficult to be oxidized to carboxylic acid, and its abundance as aldehyde is higher than those of formaldehyde and acetaldehyde. As a result, the production of butanal was 12 times (at the ionic strength of m/z 44) higher than acetaldehyde.

**Aldehydes generation from slaked lime following addition of amines**

Some amines used as emulsifying agents during slaked lime production. The TIC of the product generated when amines (2-aminoethanol, diethylamine, and trimethylamine) on the surface of slaked lime coexisted with acid gas (atmospheric conversion concentration of HCl: 110 g/m$^3$) is shown in Figs. 4(a) – 4(c). Acetaldehyde was produced from all of the amines, but formaldehyde was not generated from all of them. Some substances detected among the decomposition products of amines and reagents were considered to be impurities. When 2-aminoethanol was added, methylamine and pyrazine were detected, and the largest quantity of substances among the three amines was detected. When diethylamine was added, ethylamine and 2-aminoethanol were detected. When triethylamine was added, only ethylamine and diethylamine, which were present as impurities, were detected. The amount of acetaldehyde
hypochlorous acid and hydrochloric acid (unit: mol/m³) added; the amount of acetaldehyde produced changed when the amount of concentrated hydrochloric acid was changed. However, formaldehyde formation due to amines during chlorination in the water-treatment process, as reported by Kosaka et al. \(^{11}\) could not be confirmed. This suggests that the mechanism of aldehyde formation differs from that of formaldehyde or contributed to the immediate decomposition of the formed formaldehyde.

**Formation of aldehydes from highly reactive slaked lime (product)**

Figures 5(a) - 5(c) represent chromatograms obtained by adding 10 μL of concentrated hydrochloric acid to individual samples of slaked lime \(\alpha\) and \(\beta\), and a chromatogram obtained by adding 10 μL of ethanol to slaked lime \(\beta\). Acetaldehyde was produced in trace amounts (atmospheric equivalent (unit: mol/m³)) from the slaked lime \(\alpha\). However, 95 mg/m³ of acetaldehyde was produced from slaked lime \(\beta\), which was considered to be mainly derived from amines. Further, in slaked lime \(\beta\), the amount of acetaldehyde produced tended to increase with an increase in the amount of concentrated hydrochloric acid and hypochlorous acid. The maximum concentration of acetaldehyde reached 121 mg/m³, under the condition of the addition of 20 μL concentrated hydrochloric acid. In slaked lime \(\alpha\), no significant difference was found in the concentration of acetaldehyde when the amount of concentrated hydrochloric acid was changed. However, formaldehyde formation due to amines during chlorination in the water-treatment process, as reported by Kosaka et al. \(^{11}\) could not be confirmed. This suggests that the mechanism of aldehyde formation differs between the water and gas phases or gas-solid interface. The amount of acetaldehyde produced changed when the amount of hypochlorous acid and hydrochloric acid (unit: mol/m³) added to slaked lime \(\beta\) was increased, and is shown in Fig. 6. The aqueous solution of sodium hypochlorite and amount of concentrated hydrochloric acid added are expressed in atmospheric equivalent (unit: mol/m³). Acetaldehyde increased rapidly with the addition of 5 μL (HClO: 0.19 mol/m³, HCl: 3.0 mol/m³), and thereafter the rate of the increase decreased. The initial formation of acetaldehyde was evaluated.

Sodium hypochlorite was added to slaked lime \(\beta\) per unit weight (g) as a source of hypochlorous acid gas and concentrated hydrochloric acid was added as hydrochloric acid gas. The amount of acetaldehyde formed per mol/m³ of acids was calculated as:

\[
C_1 = \frac{C_{\text{aldehyde}} \times M_{\text{acid}} \times \rho_{\text{acid}} \times V_{\text{acid}} \times C_{\text{acid}}}{V_{\text{alcohol}} \times \rho_{\text{alcohol}}} = C_{\text{alcohol}}
\]  

where \(C_1\) is the concentration of aldehyde formed after the addition of 1 mol acid; \(C_{\text{aldehyde}}\) is the atmospheric equivalent concentration of formaldehyde or acetaldehyde formed from amine after hydrochloric acid and hypochlorous acid addition; \(\rho_{\text{acid}}, V_{\text{acid}}\), and \(M_{\text{acid}}\), respectively, represent the density, added volume, and molar mass of hydrochloric acid and hypochlorous acid; and \(C_{\text{acid}}\) is the mass percent concentration of the added acid.

The concentration of acetaldehyde formed per mol amount of alcohol added (1 mol) was calculated as:

\[
C_2 = \frac{C_{\text{aldehyde}} \times M_{\text{alcohol}} \times \rho_{\text{alcohol}} \times V_{\text{alcohol}}}{V_{\text{alcohol}} \times \rho_{\text{alcohol}}} = C_{\text{alcohol}}
\]  

where \(C_2\) is the concentration of aldehyde formed after the addition of 1 mol alcohol; \(C_{\text{aldehyde}}\) is the air-equivalent concentration of formaldehyde or acetaldehyde produced from methanol and ethanol; and \(\rho_{\text{alcohol}}, V_{\text{alcohol}}, M_{\text{alcohol}}\), respectively represent the densities of methanol and ethanol, added volume, and molar mass.

The amount of acetaldehyde formed from slaked lime \(\beta\) by hypochlorous acid and hydrochloric acid was calculated according to Eq. (2) as 371 mg/m³·mol (HClO) and 34.4 mg/m³·mol (HCl) when acids added 10 μL, respectively. Thus, the study found that hypochlorous acid species were more effective in producing acetaldehyde from amines. The concentration of aldehydes produced was 16.8 mg/m³·mol (HCl), which is nearly one-third (Fig. 5) of 50.5 mg/m³·mol (ethanol), produced by adding 10 μL of alcohol (calculated according to Eq. (3)).

Although the amount of aldehyde generated by the addition of acid was not a small value, there are few examples where amines are used as an emulsifier used in the production of highly reactive slaked lime. For this reason, it is assumed that the formation of aldehydes by alcohol is important.

In this study, the atmospheric concentration of concentrated
hydrochloric acid (to which 10 μL of alcohol was added) was 200 g/m³, and the actual hydrogen chloride gas concentration in the incinerator was about 0.5 – 2 g/m³; thus, the experiment was performed in the high-concentration region. Therefore, low-concentration conditions were tried using diluted acid and alcohol. However, since the side reaction caused by the increase in the solvent and water greatly affected acetaldehyde formation, in this study, highly reactive slaked lime was evaluated by experiments conducted under high-concentration conditions.

Conclusions

Methanol and ethanol are chemical substances that can be released into the environment at low concentrations in the final exhaust gas of waste incineration facilities. This study shows that alcohols can be easily converted to aldehydes, which are harmful. Moreover, the conversion rate of alcohols to aldehydes obtained in this study clarifies the behavior of aldehydes. But the conversion rate calculated in this study cannot be used directly to determine the amount of aldehydes generated in the final exhaust gas from waste incineration facilities as the bag filter environment reproduced in this study differs from the actual production conditions. Further, the contact time, flow rate, and catalytic effect are different. However, the one-pot evaluation method using HS-GCMS proposed in this study can be used for the initial evaluation of aldehydes unexpectedly generated in incineration facilities in the future. And besides the method developed in this study, there is no method that can easily trace the reaction in the bag filter of the waste incineration treatment facility.

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