



Combustible and incombustible speciation of Cl and S in various components of municipal solid waste

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Abstract

Chlorine (Cl) and sulfur (S) in municipal solid waste (MSW) are important reactive elements during combustion. They generate the acidic pollutants HCl and SO_x, and, furthermore, produce and suppress organic chlorinated compounds. Nevertheless, few practical reports about Cl and S content in MSW have been published. In combustion and recycling processes, both combustible Cl and S, and incombustible Cl and S species are equally important. This paper presents the results of a comprehensive study about combustible and incombustible Cl and S in MSW components, including kitchen garbage, paper, textiles, wood and leaves, plastics and small chips. By integrating this collected data with data about MSW composition, not only the overall content of Cl and S in MSW, but also the origins of both combustible and incombustible Cl and S were estimated. The average Cl content in bulk MSW was 3.7 g/kg of raw MSW, of which 2.7 and 1.0 g/kg were combustible and incombustible, respectively. The Cl contribution from plastics was 76% and 27% with respect to combustible and incombustible states. The average S content in bulk MSW was 0.81 g/kg of raw MSW, of which 0.46 g/kg was combustible and 0.35 g/kg was incombustible. Combustible S was mainly due to synthetic textiles, while incombustible S was primarily from paper.

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1. Introduction

It is clear that chlorine (Cl) and sulfur (S) in municipal solid waste (MSW) are sources of acidic pollutants during combustion, and are also the key elements in the formation of chlorinated organic compounds, e.g. dioxins (Tuppurainen et al., 1998; Gullett et al., 2000). Chlorine is essential for the formation of those compounds, while, in contrast the reductive property of sulfur dioxide (SO₂) is known to suppress the formation of chlorinated organic compounds (Raghunathan et al., 1996). For the utilization of ash for cement production, the Cl content may have to be reduced using water extraction, thereby creating another waste disposal challenge (Suto et al., 2001).

Although the importance of Cl and S in MSW has been identified, data on the content of these elements in

MSW is lacking. There is also a need to understand the linkage of total Cl and S values to the formation of acidic pollutants such as HCl and SO_x (Kubota et al., 1982). Considerable Cl remained in the bottom ash when a refuse-derived fuel was combusted (Liu et al., 2001). Moreover, Cl, as well as heavy metals, was captured in ash by addition of a sorbent (Ho et al., 2001). In these kinds of studies, the combustible and incombustible quantities of Cl and S from MSW should also be determined.

The method of determining Cl and S in MSW should also be reconsidered. Elemental and fuel analysis techniques have been adapted for MSW analysis. In principle, a sample is combusted and the residue is dissolved in an aqueous solution followed by Cl⁻ and SO₄²⁻ measurements. The quartz furnace method is employed in ISO 352, ISO 4260, JIS M 8813, JIS K 2541 and JIS Z 7302-6. The bomb method is used in ISO 1158, JIS K 7229, JIS Z 7302-6, ASTM D-2361 and JIS K 2541. The crucible incineration method (Eschka method) is used in ISO 334, ISO 587, ASTM D-2361 and JIS M 8813.

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However, careful attention must be paid to the ash content of these materials, since the residual ash can bind Cl and S. This aspect is critical since, in the quartz furnace combustion method, sample combustion in a quartz furnace is followed by gas trapping in an absorbing solution, which results in an estimation of HCl and SO_x generation through combustion. In contrast, the bomb method and crucible incineration method include Cl and S in the ash residue, consequently yielding different analytical results.

The quartz furnace method is attractive because it is able to speciate combustible and incombustible Cl and S. In our previous work, the partition of Cl and S between ash residue in the quartz vessel, on the inner surface of the quartz furnace and in the gas trapping H₂O₂ solution was studied (Watanabe et al., 2003). Consequently, an improved quartz furnace method was developed, which minimized the partitioning of Cl and S on the inner surface of the quartz furnace.

For this research, the improved quartz furnace method that we developed was applied to MSW samples collected from the Osaka City MSW survey program. The results presented in this paper include frequency diagrams as well as the representative Cl and S contents of each physical component, e.g. kitchen garbage, paper, etc. Finally, the overall distribution of combustible and incombustible Cl and S, and their origins are discussed.

2. Experiment

2.1. Sample

The MSW sample was collected as described below. One ton of MSW that had been picked up by a crane was homogeneously reduced to about 20 kg and dried at 85 °C for three days. Five categories of combustible components (kitchen garbage; paper; textiles; wood and leaves; plastics, rubber and leather (hereafter abbreviated as “plastics”)) and four categories of incombustible components (glass; stone and ceramics; ferrous steel;

non-ferrous metal) were hand-sorted. The remaining residue, which could pass through a 5 mm mesh sieve, was categorized as “small chips” and treated as a combustible component. Every combustible component was crushed until it would pass through a 1 mm screen and elemental analysis was conducted on each sample.

2.2. Improved quartz furnace method

The procedure and conditions are presented in Fig. 1 and Table 1. The apparatus is identical to that described in JIS Z 7302-6. A quartz tube of 18 mm inner diameter, and 590 mm length was used as a furnace. 200 mm of the length of the far end of the tube was filled with silica chips and kept at 900 °C by a fixed heater, while a moving heater at 600 °C was operated automatically at the front end. Air was drawn through the tube at a rate of 2 L/min as the oxidation gas. A sample mounted on a quartz vessel was placed between the moving and the fixed heaters. The moving heater started at the rear

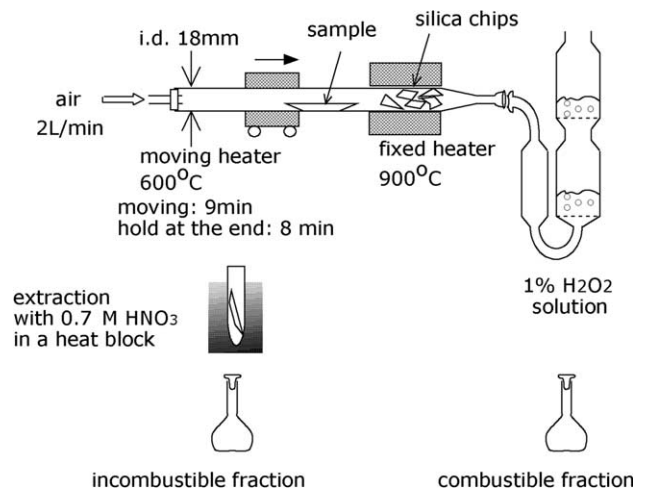


Fig. 1. Improved quartz furnace method: apparatus and procedure.

Table 1
Experimental conditions

| | Sample weight (g) | Sample combustion | | | For combustible Cl and S | For incombustible Cl and S | |
|-----------------|-------------------|-------------------|--------------------------------|-------------------------------|---|-------------------------------------|-------------------------------------|
| | | Oxidizing gas | Moving heater temperature (°C) | Fixed heater temperature (°C) | Final volume of absorbing solution (mL) | Applied 0.7 M HNO ₃ (mL) | Final volume of ash extraction (mL) |
| Kitchen garbage | 0.5 | | | | 100 | 5 | 250 |
| Paper | 0.4 | | | | 100 | 2 | 50 |
| Textile | 0.4 | Room air | 600 | 900 | 100 | 1 | 25 |
| Wood and leaves | 0.5 | 2 L/min | | | 100 | 1 | 25 |
| Plastics | 0.4 | | | | 250 | 1 | 25 |
| Small chips | 0.5 | | | | 100 | 5 | 250 |

of the quartz vessel and, after taking 9 min, finally reached the fixed heater, where it held for an additional 8 min. The combustion gas was introduced to the gas absorbing glassware which contained solution of 1% H₂O₂ (25 ml × 2).

After the combustion, the absorbing solution was diluted to 100 mL. The ash on the quartz vessel was boil-extracted with 0.7 M HNO₃ (prepared by 20 fold dilution of 14 M HNO₃) in a test tube inserted in an aluminum heat block, for half an hour, and finally diluted for ion chromatograph (IC) determination.

The weight of the sample mounted on the quartz vessel, the final volume of the gas absorbing solution, the amount of 0.7 M HNO₃ applied for boil-extraction of the ash and the final volume of extracted ash were all pre-determined from a study on the concentrations of Cl and S and ash content of the samples, as shown in Table 1.

2.3. Ion chromatograph

The concentrations of Cl and SO₄²⁻ in the sample solutions were determined with IC, the conditions of which were as follows: column: Ion Pac AS4A; eluent: 1.7 mM NaHCO₃ – 1.8 mM Na₂CO₃; suppressor regenerant: 25 mM H₂SO₄; detector: electric conductivity.

3. Results and discussion

3.1. Cl and S in each physical component

The experimental results of Cl and S in each MSW component are summarized in the frequency diagrams (Figs. 2 and 3), and in the statistical values (Tables 2

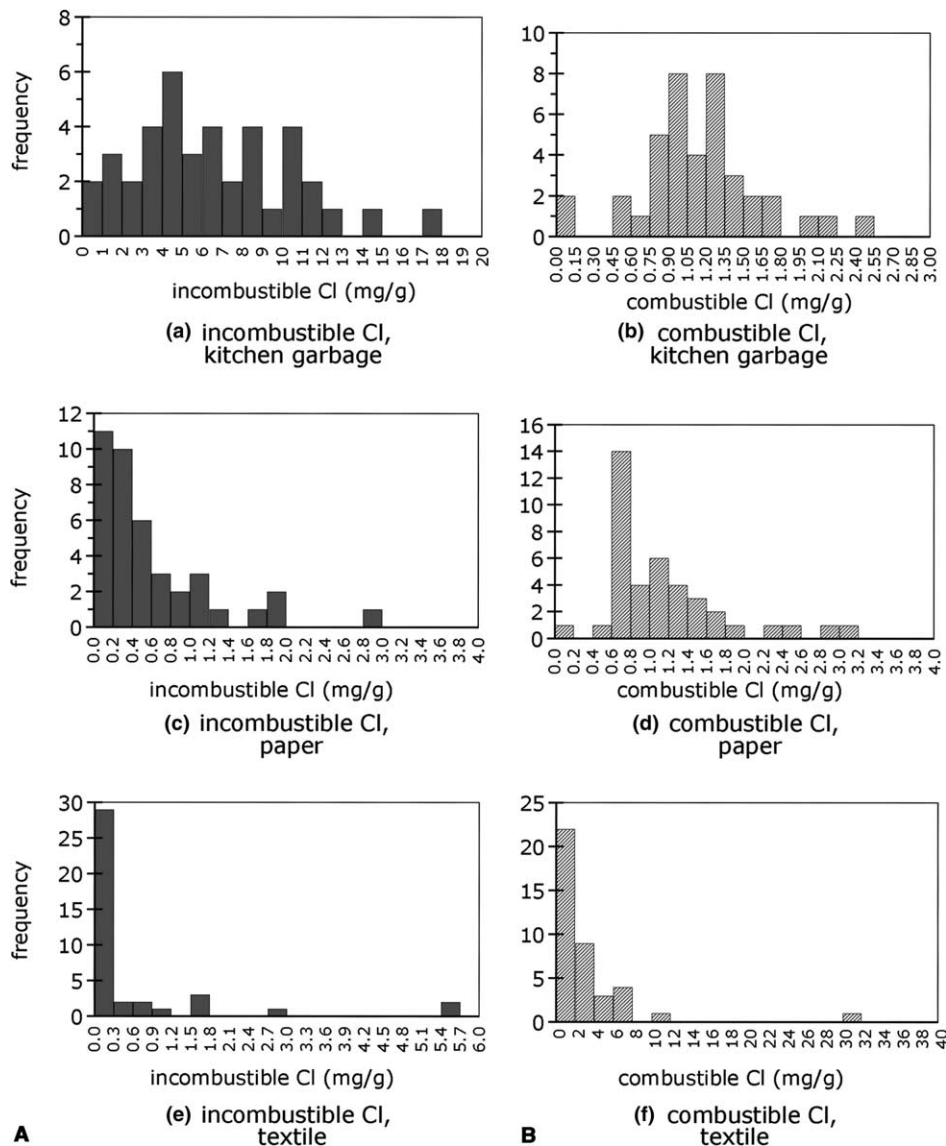


Fig. 2. Frequency diagram of Cl content in each component: (A) (1/2); (B) (2/2).

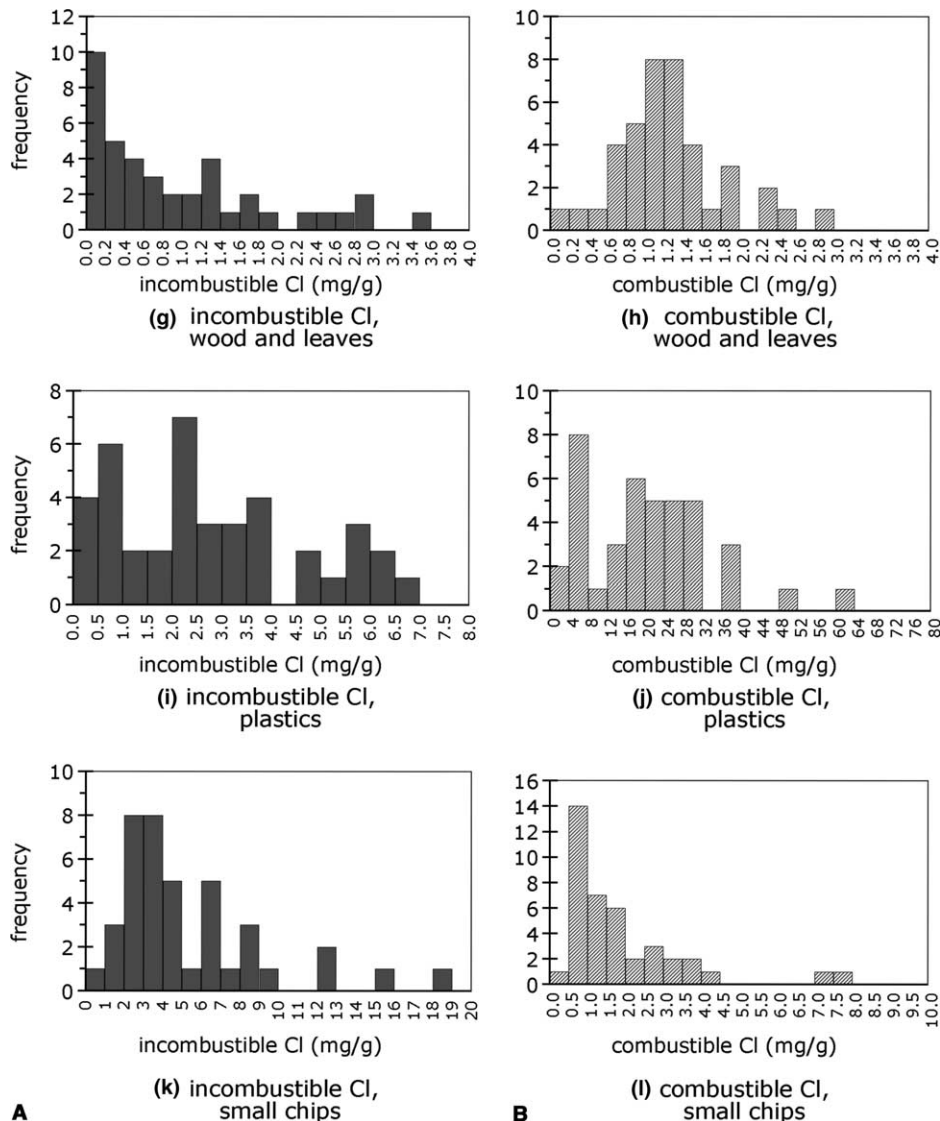


Fig. 2. (continued)

and 3). The frequency diagrams reveal asymmetric distribution, i.e. materials of extraordinarily high Cl content were sometimes found. At the same time, it is also clear that most materials contained Cl and S naturally.

The physical components could be grouped using the ratio of combustible to incombustible. Plastics involved more combustible Cl (21 mg Cl g⁻¹ on average) than incombustible Cl (2.8 mg/g), while Cl in kitchen garbage and small chips was mostly incombustible. Sulfur in textiles was mainly combustible, while most of the S in the small chips was incombustible. The other components tested contained comparable amounts of combustible and incombustible Cl and S.

3.2. Development of the experimental procedure

In our experimental method, the sample combustion was conducted at the relatively low temperature of

600 °C. The purpose was to minimize the partition of Cl on the inner surface of the quartz furnace (Watanabe et al., 2003). The higher the sample combustion temperature is, the more Cl is partitioned to the surface of the quartz furnace. The mechanism of Cl partitioning to the surface of the quartz furnace was considered to be the volatilization of alkali metal chlorides such as KCl and NaCl from the sample boat followed by re-deposit onto the surface of the quartz furnace. Hence, a relatively low temperature of 600 °C was desirable to avoid Cl loss from the boat. At the same time, Cl and S partitioning to the gas trapping solution at a sample combustion temperature of 600 °C could be considered to be highly effective.

The method of recovering Cl and S from ash residue was also examined. The simplest way was to extract the ash with distilled water, but this was sometimes inadequate, because some insoluble compounds, e.g. CaSO₄,

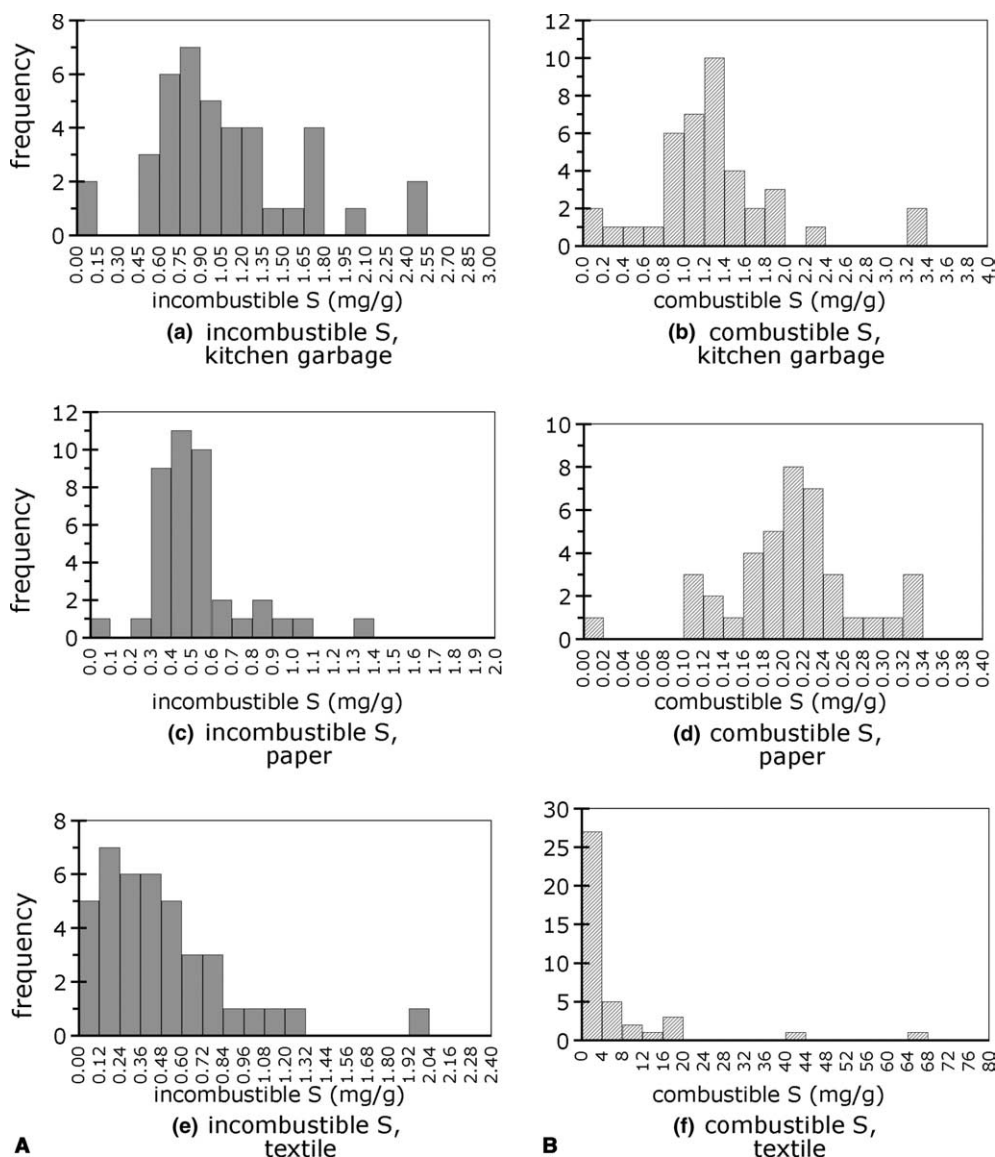


Fig. 3. Frequency diagram of S content in each component: (A) (1/2); (B) (2/2).

could not be recovered. In the next step, two extraction methods with diluted nitric acid were examined, namely room temperature 0.14 M HNO₃ and heated 0.7 M HNO₃. Ten kitchen garbage and ten paper samples were analyzed by both methods for each procedure. The results of the Cl measurements are given in Fig. 4, which reveals a difference in the extraction efficiency between the two methods. The heated HNO₃ recovered more Cl than the room temperature HNO₃. The results with S were similar to those with Cl. Although a fusion process using boric acid or sodium compounds seemed to be a more complete method, the great amount of salt accompanying this method is a great drawback for use with ion chromatographic analysis. Furthermore, blank Cl from the reagent was at a significant level. Hence, the fusion method was concluded to be unsuitable. Heat

extraction with 0.7 M HNO₃ was found to be the best available method to recover Cl and S from ash.

The above examination provided information about the reproducibility of the combustible fraction. Since all the sample types were combusted four times in the same manner, the relative standard deviation (RSD, $n = 4$) of the combustible fraction was obtained. The RSD values for combustible Cl and S in the kitchen garbage and paper are summarized in Table 4. Bearing in mind a slight problem with the homogeneity of the samples, an average RSD value of less than 10% is satisfactory.

The limit of quantification (LOQ) depends on the amounts of the samples and the final volumes of the analytical solutions, which are listed in Table 1. The IC could determine Cl and S as low as 0.1 mg/L. In the case

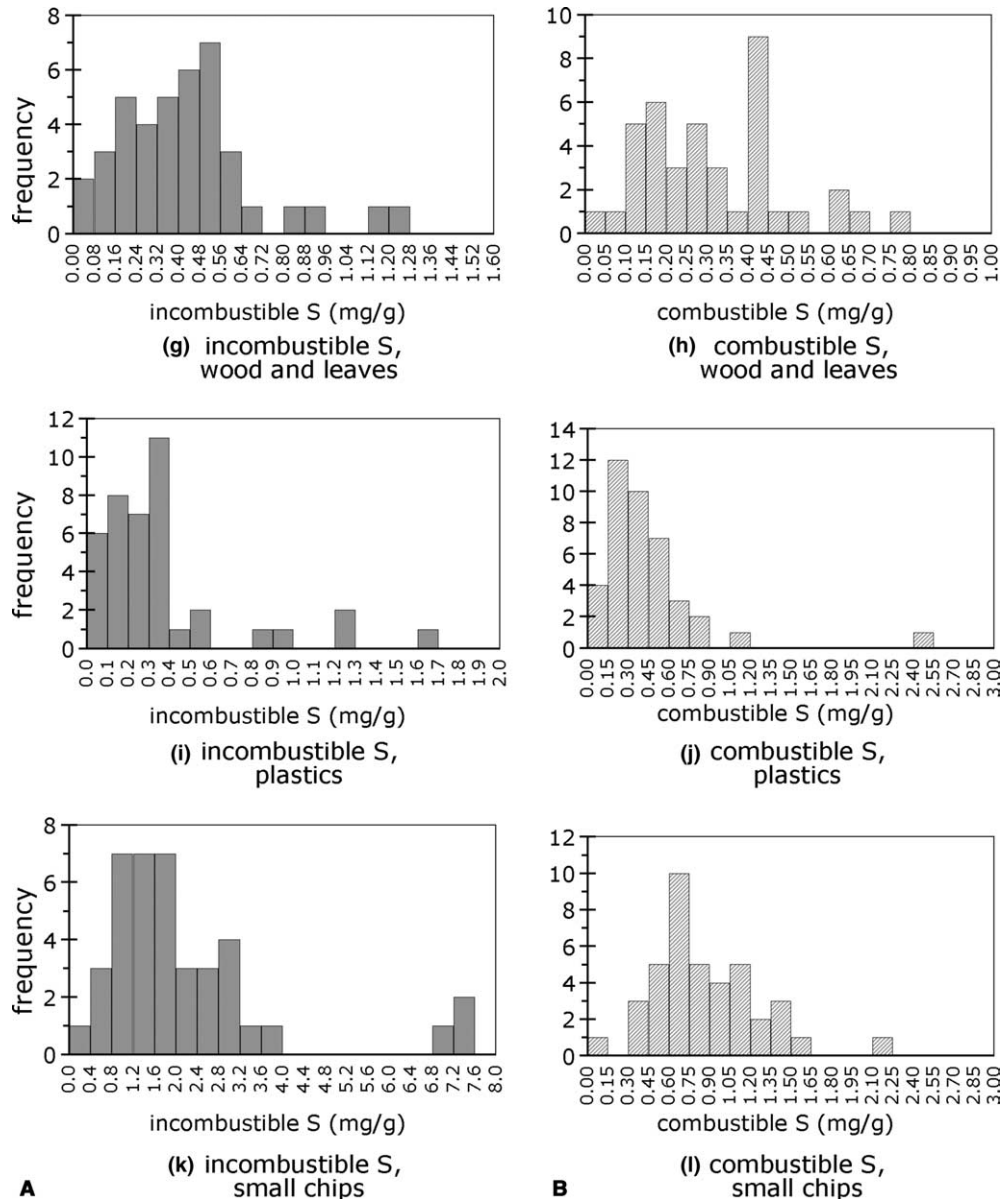


Fig. 3. (continued)

of paper, since 0.4 g of the sample was combusted to provide the analytical solution for the combustible fraction, the final volume of which was 100 mL, and the solution for the incombustible fraction was 50 mL, the LOQs were 0.025 mg/g for the combustible fraction and 0.0125 mg/g for the incombustible fraction.

3.3. Overall content of Cl and S in municipal waste

It is of practical interest to know how much Cl and S originate from each component. The data in Tables 2 and 3 show concentrations of Cl and S in the dried materials in the waste. Taking the MSW composition and using simple mean values, the overall Cl and S content of the raw MSW was estimated. The average

representative composition of MSW in Osaka City is shown in Table 5, in which overall Cl and S were calculated as follows:

- (1) Since the approximate moisture content is 37.4%, a raw MSW sample of 1000 g is divided into 374 g of moisture and 626 g of dried matter.
- (2) Since the percentage of kitchen garbage is 6.4% (dry weight basis), its mass is $626 \text{ g} \times 6.4\%/100 = 40.1 \text{ (g-dry)}$.
- (3) Combustible Cl from kitchen garbage is $40.1 \text{ g} \times 1.2 \text{ mg/g} = 48.1 \text{ mg}$.
- (4) Incombustible Cl from kitchen garbage is also calculated in the same way: $40.1 \text{ g} \times 6.8 \text{ mg/g} = 273 \text{ mg}$.

The results described in Fig. 5 reveal that the total Cl in average MSW was 3.7 g/kg of raw MSW, of which 2.7

Table 2
Statistical summary of Cl content of each component

| | | Simple mean | Geometric mean | Minimum | Maximum |
|-----------------|---------------|-------------|----------------|---------|---------|
| Kitchen garbage | Combustible | 1.2 | 1.1 | 0.52 | 2.5 |
| | Incombustible | 6.8 | 5.7 | 1.10 | 17 |
| | Total Cl | 8.0 | 7.0 | 1.6 | 18 |
| Paper | Combustible | 1.2 | 1.1 | 0.44 | 3.0 |
| | Incombustible | 0.62 | 0.41 | 0.07 | 2.8 |
| | Total Cl | 1.8 | 1.5 | 0.56 | 5.4 |
| Textile | Combustible | 3.5 | 1.6 | <0.01 | 32 |
| | Incombustible | 0.67 | 0.05 | <0.01 | 5.6 |
| | Total Cl | 4.1 | 2.4 | 0.41 | 38 |
| Wood and leaves | Combustible | 1.3 | 1.2 | 0.34 | 2.9 |
| | Incombustible | 1.0 | 0.59 | 0.08 | 3.5 |
| | Total Cl | 2.3 | 2.0 | 0.42 | 4.6 |
| Plastics | Combustible | 21 | 17 | 2.8 | 62 |
| | Incombustible | 2.8 | 2.0 | 0.04 | 7.0 |
| | Total Cl | 24 | 20 | 4.7 | 68 |
| Small chips | Combustible | 1.9 | 1.5 | 0.5 | 7.7 |
| | Incombustible | 5.5 | 4.5 | 1.2 | 18 |
| | Total Cl | 7.4 | 6.2 | 1.8 | 26 |

Unit: mg Cl g⁻¹.

Table 3
Statistical summary of S content of each component

| | | Simple mean | Geometric mean | Minimum | Maximum |
|-----------------|---------------|-------------|----------------|---------|---------|
| Kitchen garbage | Combustible | 1.4 | 1.3 | 0.33 | 3.3 |
| | Incombustible | 1.1 | 1.0 | 0.49 | 2.5 |
| | Total S | 2.5 | 2.4 | 0.96 | 4.2 |
| Paper | Combustible | 0.21 | 0.20 | 0.10 | 0.33 |
| | Incombustible | 0.54 | 0.51 | 0.29 | 1.4 |
| | Total S | 0.74 | 0.71 | 0.40 | 1.7 |
| Textile | Combustible | 6.8 | 2.4 | 0.24 | 67 |
| | Incombustible | 0.51 | 0.4 | 0.07 | 2.0 |
| | Total S | 7.3 | 3.3 | 0.53 | 67 |
| Wood and leaves | Combustible | 0.32 | 0.28 | 0.07 | 0.76 |
| | Incombustible | 0.44 | 0.37 | 0.07 | 1.2 |
| | Total S | 0.76 | 0.67 | 0.22 | 1.6 |
| Plastics | Combustible | 0.44 | 0.35 | 0.09 | 2.5 |
| | Incombustible | 0.37 | 0.26 | 0.03 | 1.7 |
| | Total S | 0.81 | 0.65 | 0.12 | 3.7 |
| Small chips | Combustible | 0.88 | 0.81 | 0.34 | 2.1 |
| | Incombustible | 2.2 | 1.8 | 0.44 | 7.3 |
| | Total S | 3.1 | 2.7 | 1.2 | 8.5 |

Unit: mg S g⁻¹.

and 1.0 g/kg were combustible and incombustible, respectively. Plastics contributed 2.05 g of combustible and 0.27 g of incombustible Cl in MSW, in other words, 76% of combustible Cl and 27% of incombustible Cl were due to plastics. Kitchen garbage contributed only 2% of combustible Cl and 27% of incombustible Cl. However, it should be noted that incombustible Cl in

other components might come from the liquids included in kitchen garbage. As a consequence, a significant amount of inorganic Cl could originate from kitchen garbage.

The other important point is the contribution of plastics (combustible: 2.05 g/kg, incombustible: 0.27 g/kg) to total Cl is 63%, which supports the argument that

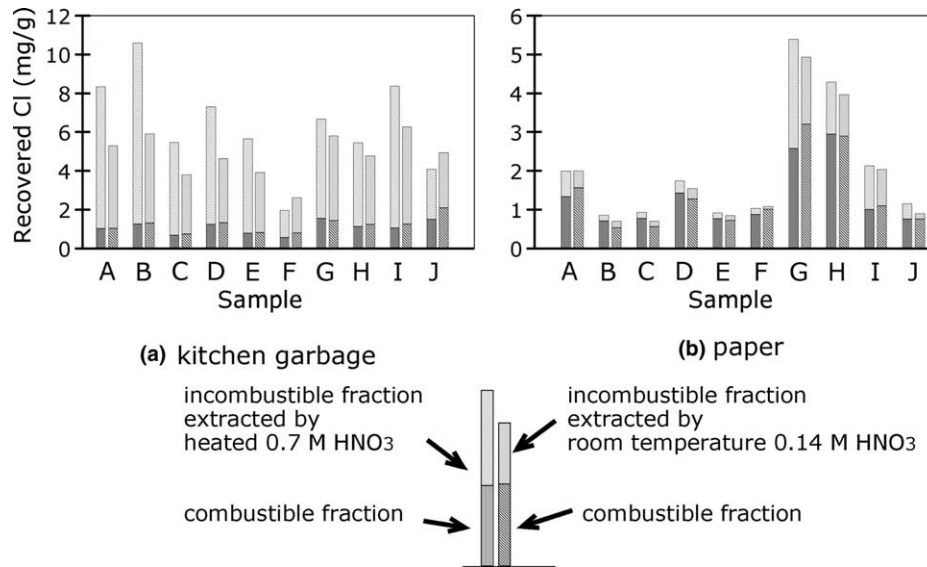


Fig. 4. Comparison of two ash extraction methods: extraction with heated 0.7 M HNO₃ and room temperature 0.14 M HNO₃.

Table 4
Reproducibility of combustible fraction

| | Relative standard deviation (RSD) | | |
|-----------------------|-----------------------------------|---------|---------|
| | Average | Minimum | Maximum |
| Cl in kitchen garbage | 7.1 | 1.5 | 18.5 |
| Cl in paper | 9.2 | 1.2 | 16.5 |
| S in kitchen garbage | 7.2 | 2.4 | 12.1 |
| S in paper | 6.6 | 2.8 | 12.0 |

$$\text{RSD} = \text{SD} (n) / \text{average} \times 100 (\%), n = 4.$$

Cl in MSW incineration could be reduced significantly if plastics were removed. Even if all plastics were excluded from municipal waste, however, 37% of the Cl would remain.

Average S in MSW was 0.81 g/kg of raw waste, of which 0.46 and 0.35 g/kg were combustible and incom-

Table 5
MSW composition

| | |
|--|------|
| <i>Proximate composition (%)</i> | |
| Moisture | 37.4 |
| Ash | 15.6 |
| Volatile matter | 47.0 |
| <i>Physical composition (dry base) (%)</i> | |
| Kitchen garbage | 6.4 |
| Paper | 46.5 |
| Textile | 6.0 |
| Wood and leaves | 5.9 |
| Plastics | 15.6 |
| Small chips | 5.8 |
| Glass | 5.4 |
| Stone and ceramics | 2.4 |
| Ferrous metal | 4.3 |
| Non-ferrous metal | 1.7 |

MSW composition: Osaka City FY 1998.

combustible, respectively. Most sulfur is from textiles (combustible) and paper (incombustible), as shown in Fig. 6. Sulfur in textiles is thought to be from synthetic textiles, however, it should be noted that S-rich textiles are not found frequently, as shown in Fig. 3(f). Incombustible S in paper is thought to be from sulfates from the paper making process (actually lignosulfates), which is a relatively constant ingredient.

4. Conclusions

Chlorine (Cl) and sulfur (S) are key elements for municipal waste incineration. The analytical procedure we developed enabled combustible and incombustible speciation of Cl and S. The samples were combusted in a quartz furnace at 600 °C, which generated flue gas and a residual ash. The Cl and S in the flue gas were considered to be combustible and those in the residual ash to be incombustible. The relatively low combustion temperature of 600 °C was able to minimize the volatilization loss of alkali metal chlorides. The recovery of Cl and S from the residual ash was conducted by heat extraction with diluted HNO₃, which was the best available extraction technique usable with ion chromatographic determination.

This method was applied to various combustible physical components of municipal waste: kitchen garbage, paper, textiles, wood and leaves, plastics and small chips. Representative values of combustible and incombustible Cl and S content in those physical components were obtained. Integrating the content values and the representative municipal waste composition, the levels and sources of Cl and S in municipal waste were estimated.

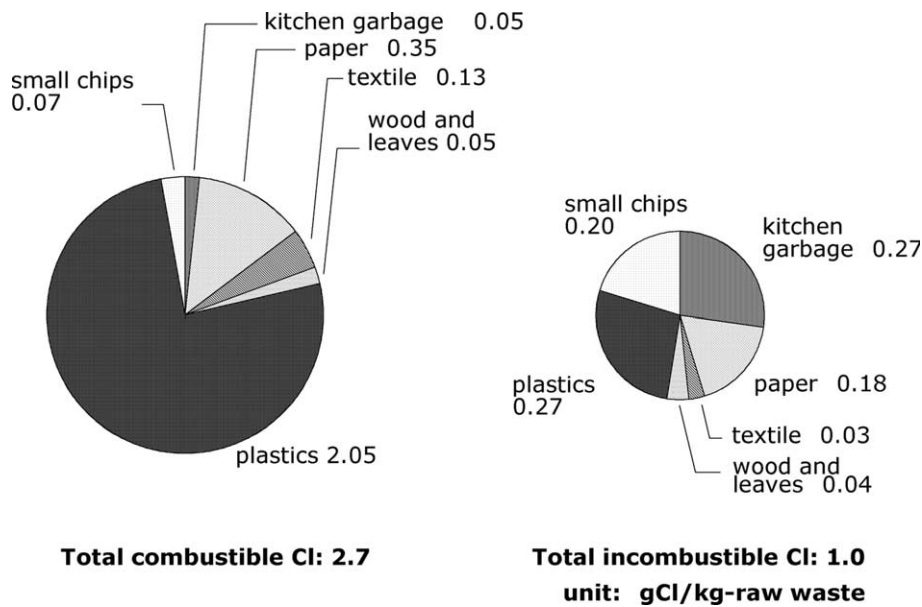


Fig. 5. Occurrence of combustible and incombustible Cl in MSW from each physical component.

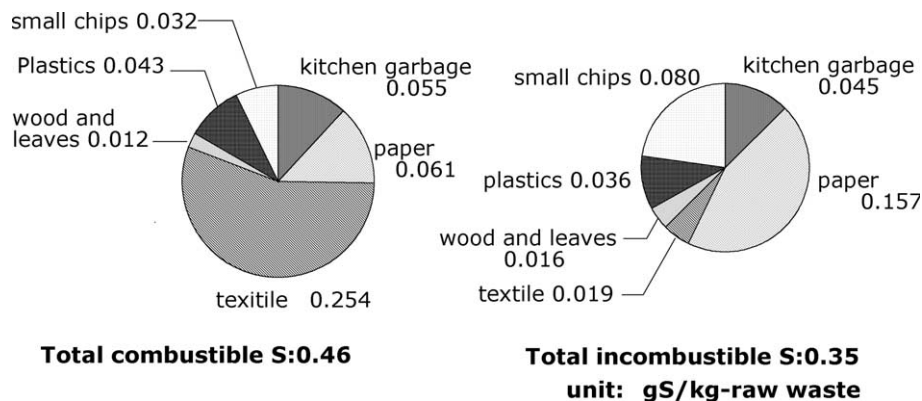


Fig. 6. Occurrence of combustible and incombustible S in MSW from each physical component.

Average Cl content in bulk MSW was 3.7 g/kg of raw MSW, of which 2.7 and 1.0 g/kg were combustible and incombustible, respectively. Plastics contributed 76% and 27% of the combustible and incombustible Cl amounts, respectively. The average S content in bulk MSW was 0.81 g/kg of raw MSW, of which 0.46 and 0.35 g/kg were combustible and incombustible, respectively. Combustible S was mainly due to some synthetic textiles, while incombustible S was primarily from paper.

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