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Identification of toxic PAH compounds in emitted particulates from incineration of urban solid wastes

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Abstract

Typical urban solid wastes, containing plastic components such as PVC, ABS, PE, PP, PS and PPMA, are employed in the investigation of PAH compounds and their respective mutagenicity in the particulates emitted from the laboratory-scale incinerators. Types of incinerator (one or two-stage) and incineration temperature (400–1100°C) are considered as the two major factors for the incineration tests. Results from the incineration tests indicated that the major PAHs in the particulates vary with operating conditions in the laboratory-scale incinerator. The mutagenicity in the emitted particulates was found to be significantly higher when the incineration temperature was controlled between 700 and 900°C.

1. Introduction

Incineration [1,2] is a process of thermal decomposition via oxidation to convert a solid waste to a less bulkly or non-noxious material. The principal products of incineration in terms of volume are CO_2, H_2O and ashes; while those in terms of environmental concerns are compounds containing sulfur, nitrogen, halogens, heavy metals and polynuclear aromatic hydrocarbons (PAHs). The PAHs [3–5], which are known to be mutagenic or carcinogenic, are commonly generated from incomplete combustion of solid waste.

The propensity to form PAHs is closely related to the types of incinerator, temperature, residence time, supply of oxygen and the nature of solid waste in the incineration process. The fundamental mechanisms [6] involving PAH formation in the incineration process are oxidation, pyrolysis, nucleation, coagulation and aggregation. Furthermore, the formed PAHs can be condensed and adsorbed onto the emitted particulates, which will diffuse to the atmosphere.

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As mentioned in the above, we are much concerned about the mutagenicity or carcinogenicity of some PAHs. What is more, certain substituted PAHs seem to exhibit direct mutagenic or carcinogenic activity. Thus, one of the objectives of this study is to understand the major PAH compounds with their associated toxicity level in the particulates emitted from incineration of the urban solid waste.

2. Materials and methods

Solid waste containing paper (5.480 g), textile (1.546 g), wood (0.468 g), garden trimmings (0.544 g), garbage (5.64 g), rubber (0.182 g), PE (1.19 g), PVC (0.426 g), PP (0.156 g), PS (0.146 g) and ABS (0.131 g) were synthesized as the typical urban solid waste (USW) on which to perform the incineration test. In each test, 2.0–5.0 g USW were weighed and introduced to the one-stage incinerator (42 cm (L) × 22 cm (D)) and two-stage incinerator (60 cm (L) × 35 cm (D)), respectively. For the one-stage incineration tests, the temperature was controlled between 400 and 1100 °C; while for the two-stage incineration tests, the preheating temperature was operated at 400 or 600 °C and the follow-up combustion temperature was maintained at 900, 1000 and 1100 °C, respectively.

In order to keep the air particulate samples from contamination, a quartz tube of dimension 100 cm length and 42 cm inside diameter was inserted into the furnace. All the air particulate samples were collected onto glass-fiber filters by a vacuum pump under the "complete combustion" condition where the residence time was for at least 90 s with a fixed flow rate of 20 l/min.

The emitted particulates collected on the glass fibers were extracted at 45 °C for 16 h in a Soxhlet apparatus with 250 ml dichloromethane. The extract was evaporated to dryness with a rotary evaporator. The residue was dissolved in 0.4 ml dichloromethane. An aliquot of 0.2 ml extract was used to conduct the mutagenicity test according to the proposition by Ames et al. [7]. The rest of the dichloromethane extract was first purified by silica gel TLC plate and then concentrated to determine the PAH contents, including fluorene (Flu), pyrene (Pyr), benzo[b]fluoranthene (BbF), benzo[a]anthracene (BaA), chrysene (Chr), bezo[e]pyrene (BeP), benzo[ghi]perylene (Bghi), benzo[a]pyrene (BaP), perylene (Per), phenanthrene (PhA), 2,3-benzofluorene (Ben) and triphenylene (Tph) by a computer controlled GC/MS system (Hewlett Packard Model 5984A) [8]. The emitted gas was also continuously detected by the CO monitor (IMR3010P).

3. Results and discussion

Figures 1–4 show the concentrations of 3-ring to 6-ring PAHs in the particulates emitted from incineration of the urban solid waste (USW) at temper-

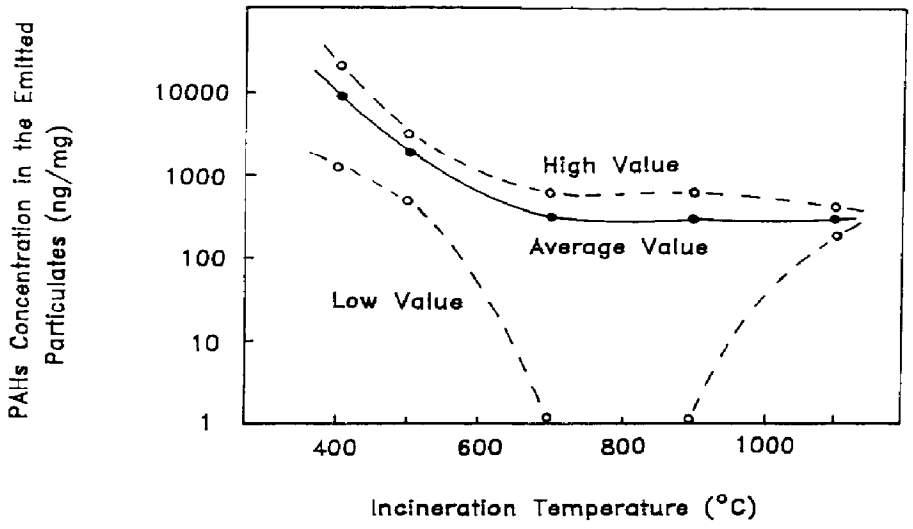

Fig. 1. The 3-ring PAHs concentration (Flu, Pha) in emitted particulates from incineration of urban solid waste at various incineration temperatures.

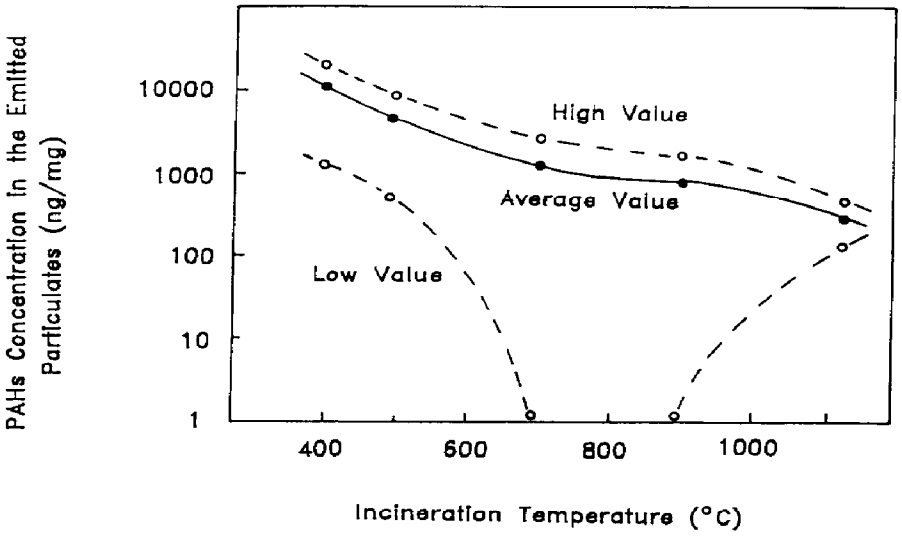

Fig. 2. The 4-ring PAHs concentration (BaA, Chr, Pyr, 2,3-Benzo, Tph) in emitted particulates from incineration of urban solid waste at various incineration temperatures.

atures between 400 and 1100°C, respectively. It is clearly depicted in Fig. 1 that the average concentration of 3-ring PAHs abruptly decreases as the incineration temperature is increased from 400 to 700°C. Afterwards, the 3-ring PAHs remained at a stable level when the incineration temperature was kept between 700 and 1100°C. A relatively higher fluctuation of 3-ring and 4-ring PAHs concentration is observed at an incineration temperature between 700

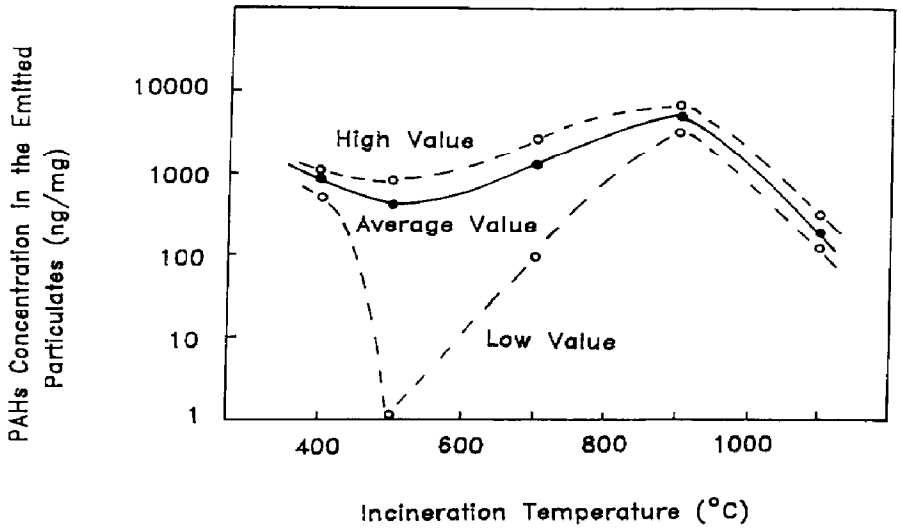

Fig. 3. The 5-ring PAHs concentration (Bep, Bap, BbF, Per) in emitted particulates from incineration of urban solid waste at various incineration temperatures.

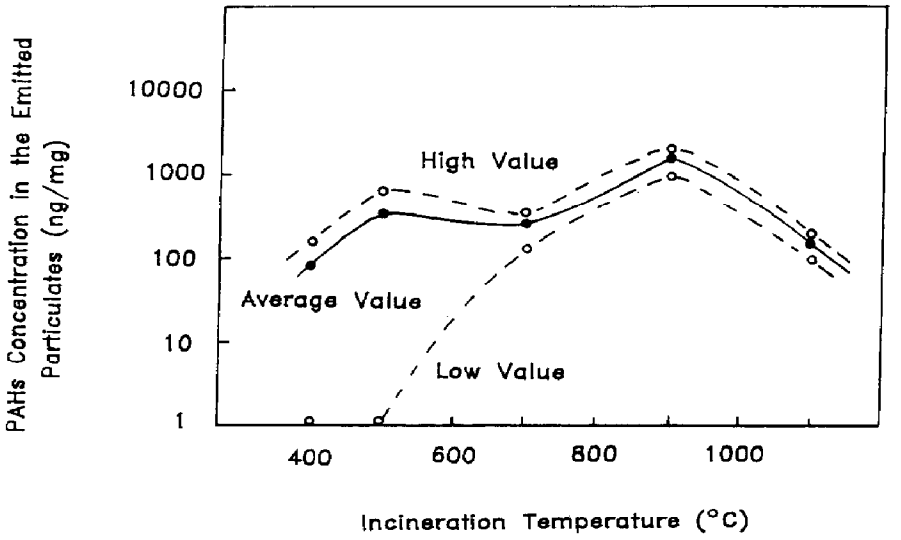

Fig. 4. The 6-ring PAHs concentration (Bghi) in emitted particulates from incineration of urban solid waste at various incineration temperatures.

and 900°C, which indicates that constant production of 3-ring and 4-ring PAHs at these temperatures is hard to achieve.

The wider range of concentrations of 3-ring (or 4-ring) PAHs presented in Fig. 1 (or Fig. 2) also suggests a very complicated combustion phenomena, i.e. oxidative pyrolysis, nucleation, condensation, coagulation and aggregation should coexist especially at incineration temperatures between 700 and 900°C.

On the other hand, Figs. 3 and 4 demonstrate that the concentrations of both

5-ring and 6-ring PAHs gradually increase as the incineration temperature approaches to 900°C. The concentration of 5-ring (or 6-ring) PAHs markedly decreased when the incineration temperature was maintained between 900 and 1100°C. The range of concentration of the 5-ring (or 6-ring) PAHS was drastically decreased as the incineration temperature was increased. In general, the above findings shown in Fig. 3 (or Fig. 4), are not similar to that observed in Figs. 1 and 2. These inconsistent observations can be interpreted by the hypothesis that a certain portion of the solid waste should be degraded through a pyrolysis and cracking process at lower incineration temperatures (400–500°C) and results in the production of a higher level of 3-ring or 4-ring PAHs. The formation of 5-ring or 6-ring PAHs, through reactions including oxidative pyrolysis, nucleation and aggregation [6], became more spontaneous at the expense of thermal energy (700–900°C). However, with a sufficient supply of thermal energy at 1100°C in the incineration process, complete oxidation (or destruction) is expected to be accomplished and resulted in decreasing the formation of PAHs, which is shown in Figs. 1–4.

From these very interesting findings, it should be noted that incomplete combustion or recombination of hydrocarbons resulted in the production of toxic PAH compounds. These compounds presumably exert a great deal of toxicity at incineration temperatures from 800 to 900°C, which is the general operation practice currently conducted by municipal solid waste incinerators throughout the world. These hypotheses could be reconfirmed by the results of the Ames test.

Figure 5 shows the mutagenicity associated with particulates emitted from incineration of urban solid waste at temperatures ranging from 400 to 1100°C.

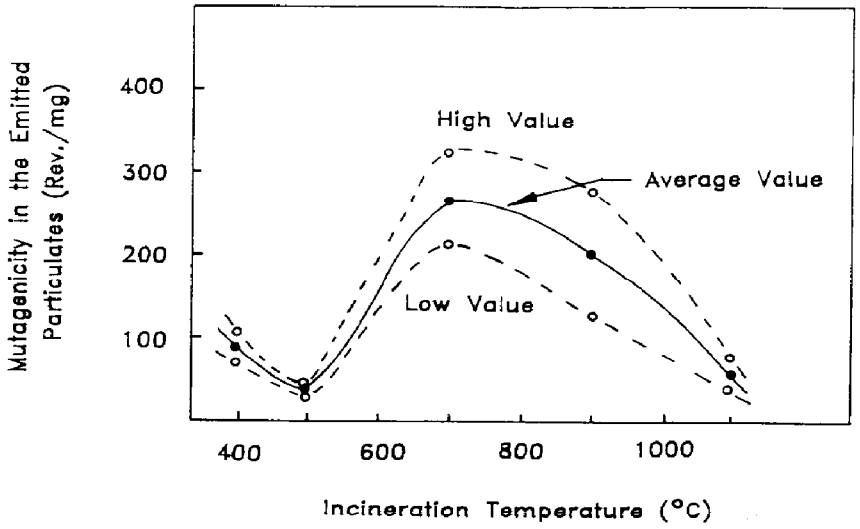

Fig. 5. Mutagenicity in emitted particulates from incineration of urban solid waste in one-stage incineration with temperatures from 400–1100°C.

It is obvious from Fig. 5, that the highest and lowest mutagenicity associated with the emitted particulates were observed at 700 and 1100°C, respectively. This strongly suggests that the incineration temperature should be controlled at 1100°C, where complete destruction of USW can be accomplished to decrease the toxicity of the emitted particulates.

Figure 6 presents the effects of one-stage and two-stage incineration processes on the mutagenicity associated with the emitted particulates. The data, shown in Fig. 6, indicate that there was no certain criterion for selecting the types of incinerator provided that the combusion (or clean-up) temperature was held at 900°C. Beyond that, from the mutagenicity point of view, there is no doubt that the two-stage incineration process, i.e. 600/1000°C and 600/1100°C, is superior to the one-stage incineration process. In addition, the two-stage incineration process operated at 600/1100°C also offers the merit of providing a relativity stable or consistent toxicity level in the emitted particulates which quite fulfilled the QA/QC monitoring program currently being executed in the USW incinerator.

In the literature, it was reported that CO monitoring data of air emission might provide the base-line information for estimating the concentration of noxious compounds, such as dioxins, generated from the combustion process. In this investigation, we demonstrate that the emitted CO concentration can be correlated with the PAH_6 concentration in the emitted particulates, which

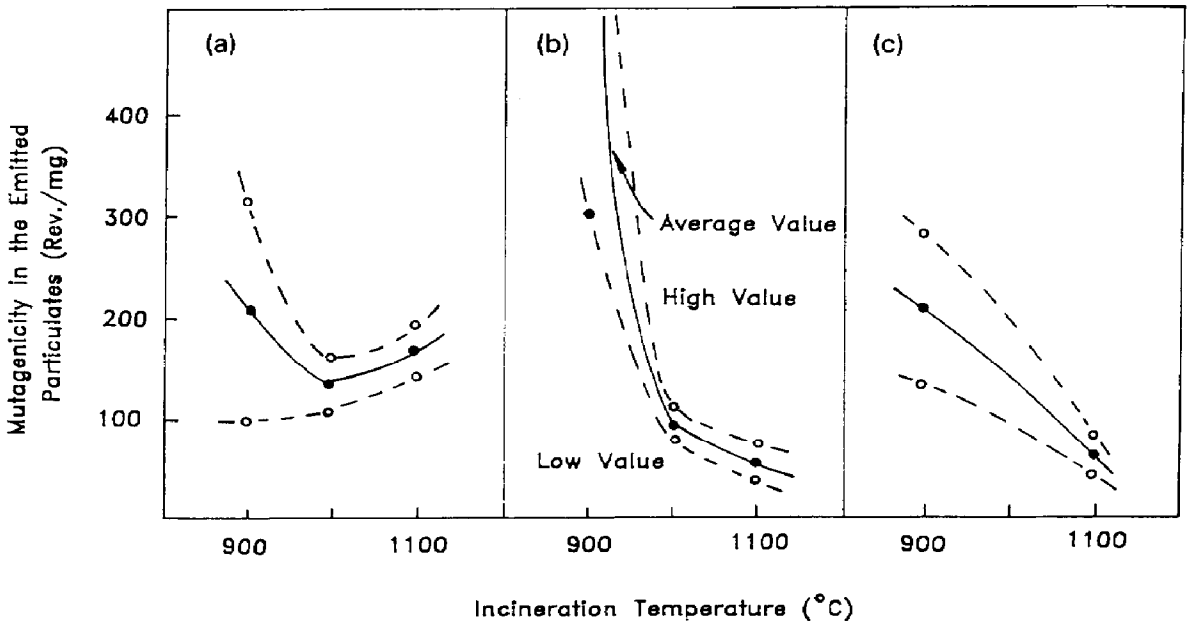

Fig. 6. Comparison of mutagenicity in emitted particulates from incineration of urban solid waste in one-stage and two-stage incinerators with clean-up temperature from 900 to 1100°C. (a) Two-stage incineration test, preheating at 400°C; (b) two-stage incineration test, preheating at 600°C; and (c) one-stage test.

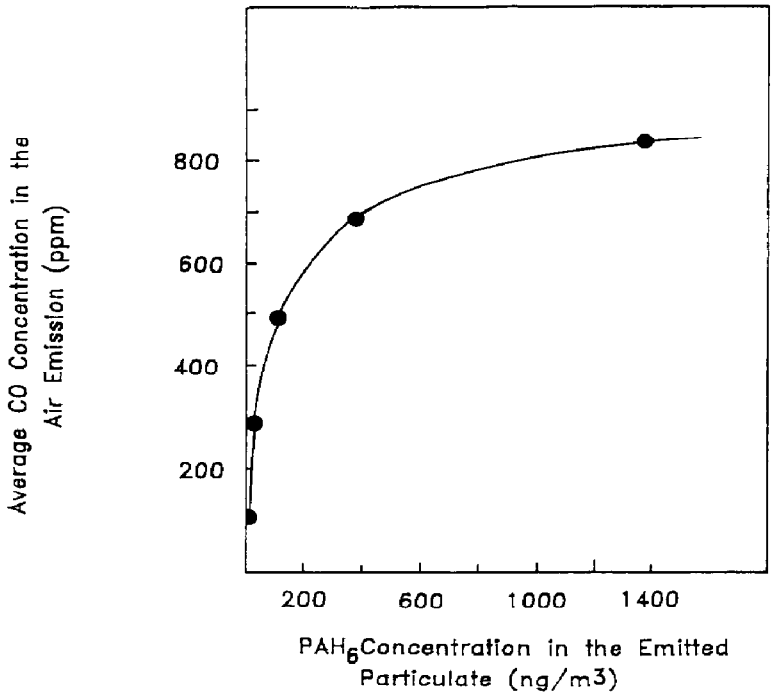

Fig. 7. Correlation between average CO concentration in air emissions and PAH concentration in emitted particulates from incineration of urban solid waste in the two-stage incinerator.

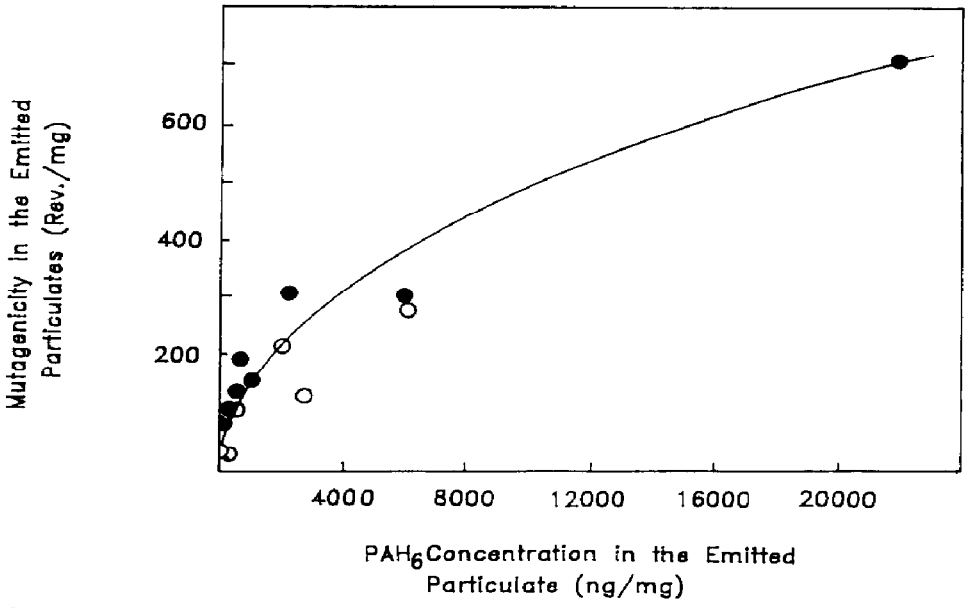

Fig. 8. Correlation between PAH_6 concentration and mutagenicity in emitted particulates from incineration of urban solid waste at various incineration temperatures. (●) Two-stage incineration, preheating at 400 or 600°C, Cleanup at 900, 1000 or 1100°C; (○) One-stage incineration with temperatures ranging from 400–1100°C.

is shown in Fig. 7. With this unique finding, we suggest that the monitoring of CO concentration in air emission should be a rapid method for predicting the toxicity level in the emitted gas if long-term continuous monitoring data of CO and PAHs is made available.

Our previous study [9] indicated that there was a strong correlation between PAH_6 (or PAH_{14}) concentration and mutagenicity in the emitted particulates from incineration of a specific chemical compound, such as ABS or PVC. Although the components are very complex in the USW used in this study, the correlation between the PAH concentration and mutagenicity in the emitted particulates (Fig. 8) is reasonably good, no matter what incineration temperature and type of incinerator were adopted. This strongly suggests that the measurement of PAH_6 should be regarded as a very important parameter for evaluating the toxicity level in the emitted particulates from incineration of the USW.

4. Conclusion

The results of the incineration tests presented in this paper indicate that the majority of PAHs occurring in the particulates vary with their respective operating conditions in the laboratory-scale incinerator. A relatively higher concentration of 3-ring and 4-ring compounds of PAHs, i.e. fluorene (Flu), pyrene (Pyr) and 2,3-benzo[e]fluorene (Ben) were formed under one-stage incineration with the temperature ranging from 400 to 500°C. The species of PAH would shift to 5-ring compounds such as benzo[b]fluoranthene (BbF), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP) and benzo[ghi]perylene (Bghi) when the incineration temperature went up to 900°C. It is noted, however, that these major PAH compounds are drastically decreased as the temperature approaches to 1100°C.

On the other hand, the results of the two-stage incineration test revealed that the incineration temperature controlled in the combustion zone and gasification zone exerted marked effects on the species of PAHs in the particulate samples. Although the incineration tests were controlled at the same combustion temperature, the concentration of BbF, BeP and BaP in the particulates for two-stage incineration (600/900°C) was higher than those generated by one-stage incineration (900°C).

The mutagenicity of the emitted particulates indicates a significantly higher value when the incineration temperature was controlled between 700 and 900°C. The mutagenicity of these air particulate samples agree reasonably well with their respective PAH_6 concentration.

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