

Polycyclic aromatic hydrocarbons (PAHs) and mutagenicity in air emissions from the two-stage incineration of polystyrene with various metallic salt additives

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Abstract

The yield of 14 PAHs and soots were more with BaCl₂ or NaCl additive than those without metallic chloride additives. This indicated that metallic chloride additives could promote the reaction sequence towards the growth and coagulation reaction of soots from PS pyrolysis. When the second-stage temperature increased to the critical temperature, black tar formed and the concentration of 14 PAHs was 10 µg/g PS. Pha, Flu and Pyr were major species found among the 14 PAHs. Log *K* values, the ratios between the PAHs in gas phase and the PAHs in solid phases (per particulates weight; 1/mg) increased as the stage-two pyrolysis temperature increased. When the stage-two incineration system was controlled at 900 °C as were various oxygen supplies, the maximum value of log *K* occurred at 0.0525 O₂ (nl/min) and log *K* value decreased as the oxygen supply increased. When oxygen supply was increased from 0 to 0.210 nl/min, the mutagenicity of particulates extracts from the PS incineration with metallic chloride additives was still more stronger.

Keywords: PAHs; Mutagenicity; Incineration; Polystyrene; Air emission

1. Introduction

With the increase in environmental consciousness among the people, traditional solid-waste handling methods, landfill and incineration, are meeting with increasing public resistance. Especially, air emissions from incineration are now releasing not only traditional air pollutants, but also air toxics, such as polycyclic aromatic compounds (PAHs), dioxins, and furans.

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PAHs, which are thought to be the precursors of soots and have also been known to be mutagenic or carcinogenic, after being metabolized, are commonly produced from the incomplete combustion processes [1–6]. The formation of PAHs and soot particulates in the incineration of organic compounds not only depends on temperature, residence time and oxygen supply, but also depends on additives, e.g. Cl_2 and metallic salts. Since complex mechanisms are involved in the incineration (or combustion) processes, their influence on PAHs and soot particulates formation is not yet clearly understood and various hypotheses, such as ionic chemical mechanisms, hydroxyl radical equilibrium and electrostatic effects are proposed based on various experimental systems and results [7–13].

Dependence of PAHs-induced mutagenicity on the bay region of the molecule and on the activating cytochrome P-450 enzyme has already been studied [14]. The results showed that the mutagenic activity of PAHs without a bay region was largely independent of the source of activating enzyme. Some researchers indicated that nucleophilic epoxides were formed from a metabolic oxidation of PAHs and then the epoxide ring would react with a nucleophilic group in cellular DNA. With its DNA thus altered, the cell was unable to reproduce normally [15]. According to the experimental results of a prototype/laboratory-scale rotary kiln under suboptimal operation conditions, Demarini suggested that the mutagenic emission factors may depend as much as or more on the operating conditions of the incinerator than on the feed stock [16].

The objectives of this research work are to investigate the mutagenicity and PAHs in air emissions from the incineration of polystyrene with various metallic salt additives under various stage-two pyrolysis temperatures and oxygen supplies.

2. Materials and methods

Polystyrene (PS) (0.2 g) was incinerated at various temperatures and oxygen supplies in a two-stage incinerator. The two-stage incinerator consisted of two furnaces and two quartz tubes ($D = 3$ cm, $L = 30$ cm and $L = 50$ cm). The feed gas, which consisted of oxygen and nitrogen, was first introduced through two tubes ($D = 5.0$ cm, $L = 30$ cm) containing 1 M BaCl_2 or 3 M NaCl solution, and then carried BaCl_2 (1.3×10^6 mmol/s) or NaCl (1.1×10^5 mmol/s) into the second-stage incinerator. The feed rate was controlled at 2.0 nl/min and at various oxygen ratios by using the flotation flowmeter and needle valves. The rate of temperature increase in the stage-one incinerator was controlled at 35–40 °C/min, and the maximum temperature was controlled at 500 °C. The temperature in the stage-two incinerator was controlled at 700 °C to 1200 °C. The theoretical residence time was 2–4 s.

The glass-fiber filter was used for sampling the particulates and PAHs which were defined in the solid phase. PUF (polyurethane foam) was used for sampling the PAHs which were defined in the gas phase. The sampling time was 5 min and the sampling flow time was 5 nl/min. The samples were pretreated in a series process: extraction, concentration and purification. Then the GC/MS (HP5890-11, HP G1034C MS Chemstation; NIST/EPA/NIH Mass Spectral Database-Envelop)

Table 1
The name and characteristics of PAHs

Name	Chemical formula	Molecular weight	Melting point (°C)	Boiling point (°C)	Carcinogenicity	Chemical structure
PhA (phenanthrene)	C ₁₄ H ₁₀	178	101	340	–	
Flu (fluoranthene)	C ₁₆ H ₁₀	202	110	393	–	
Pyr (pyrene)	C ₁₆ H ₁₀	202	156	404	–	
Ben (benzo[b]fluorene)	C ₁₇ H ₁₂	216	N.D.	N.D.	–	
BaA (benz[a]anthracene)	C ₁₈ H ₁₂	228	158	435	+	
Chr (chrysene)	C ₁₈ H ₁₂	228	254	448	±	
Tri (triphenylene)	C ₁₈ H ₁₂	228	199	425	–	
BbF (benzo[b]fluoranthene)	C ₂₀ H ₁₂	252	N.D.	393	++	
BeP (benzo[a]pyrene)	C ₂₀ H ₁₂	252	178	312	–	
BaP (benzo[e]pyrene)	C ₂₀ H ₁₂	252	179	496	+++	
Pr (perylene)	C ₂₀ H ₁₂	252	273	500	–	
DbA (dibenz[a,h]anthracene)	C ₂₂ H ₁₄	278	266	535	+++	
IP (indeno[1,2,3-cd]pyrene)	C ₂₂ H ₁₂	276	N.D.	534	+	
BghiPR (benzo[g,h,i]perylene)	C ₂₂ H ₁₂	276	273	542	–	

Note: –, Not carcinogenic; +, uncertain or weakly carcinogenic; ++, carcinogenic; +++ very strongly carcinogenic.

Table 2
The regression equations of GC/MS calibration curves of 14 PAHs

PAH	Regression equation	R^2
1. PhA	$y = 2.551 \times 10^8 x + 1.362 \times 10^5$	0.984
2. Flu	$y = 4.753 \times 10^8 x + 3.511 \times 10^4$	0.984
3. Pyr	$y = 2.793 \times 10^8 x - 2.314 \times 10^4$	0.996
4. Ben	$y = 1.095 \times 10^8 x - 4.005 \times 10^5$	0.998
5. BaA	$y = 1.700 \times 10^8 x - 1.681 \times 10^5$	0.990
6. Tri + Chr	$y = 5.208 \times 10^8 x - 1.532 \times 10^5$	0.999
7. BbF	$y = 1.818 \times 10^8 x - 1.078 \times 10^5$	0.998
8. BeP	$y = 1.647 \times 10^8 x - 6.384 \times 10^5$	0.999
9. BaP	$y = 3.363 \times 10^8 x - 3.876 \times 10^5$	0.997
10. Pr	$y = 1.759 \times 10^8 x - 5.394 \times 10^4$	0.999
11. IP	$y = 2.141 \times 10^8 x - 2.451 \times 10^5$	0.999
12. BghiPr	$y = 2.310 \times 10^8 x - 1.001 \times 10^5$	0.992
13. DbA	$y = 1.214 \times 10^8 x - 1.592 \times 10^5$	0.997

Note: (1) y , signal area; x : PAHs(ug).

(2) R^2 , correlation coefficient.

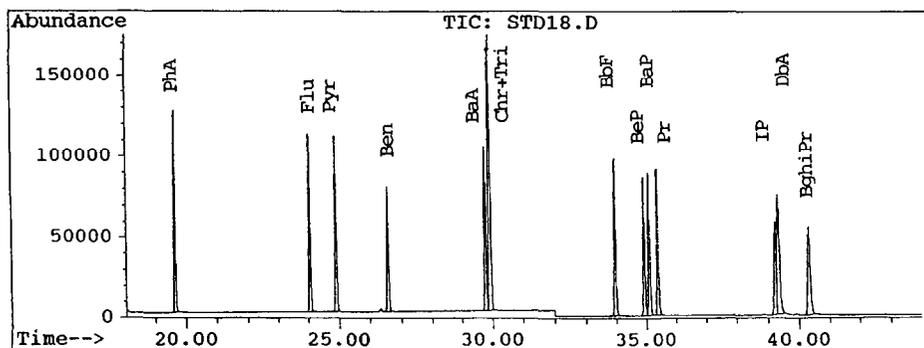


Fig. 1. GC/MS spectrum of 14 PAHs standards.

was used to analyze the 14 species of PAHs as shown in Tables 1, 2 and Fig. 1. During the extraction process, samples were placed and extracted in a soxhlet extractor with 250 ml of dichloromethane at 40 °C for about 16 h. After the extraction process, the dichloromethane residue was concentrated to 1–2 ml by using a rotary evaporator. The extract residue was purified with 100 ml of hexane–dichloromethane (7:3, v/v) in the tube purifier ($D = 1$ cm, $L = 20$ cm) which was packed with 2 g of activated aluminum and 3 g of silica gel. Finally, the purified samples were concentrated to 2 ml by using a rotary evaporator, and dried to 1 ml by using nitrogen.

The mutagenic activity of the particulates and PUF extracts were tested by the Ames Salmonella/microsomal assay system [17, 18]. From the mutagenicity research of ambient particles, it was noted that the mutagenic response of strain TA98, which was used to detect frame-shift substitution mutation, was significantly higher than that of strain TA100, which was used to detect base-pair

substitution mutation, upon incubation with the dichloromethane extract residue of airborne particulates. Thus, *Salmonella typhimurim* strain TA98 was employed to carry out the mutagenicity test in this study.

0.8 ml of DMSO was added to the dried sample in the vial. The aliquot of sample extracts in DMSO was placed in a test tube containing 2 ml of molten top agar supplemented with a 0.1 ml test solution, 0.1 ml of an overnight broth culture of the tester strain, and with or without 0.5 ml of S9 mixture. The S9 homogenate was prepared from the liver of Sprague–Dawley male rats pretreated for 5 days with Aroclor 1254 (500 mg/kg body weight) according to Maron and Ames et al. [17]. After 2 days incubation of the culture plates at 37 °C, histidine revertants of TA98 were scored.

3. Results and discussion

In our investigation, when the thermal temperature of the first-stage incinerator was at 350–450 °C, polystyrene was decomposed by the mechanisms of random-chain scission and end-chain scission. The long chain of polymer structure was broken down to a shorter-chain structure, i.e., styrene monomer, dimer, trimer and toluene.

When the intermediate products from the first-stage incinerator were introduced to the second-stage incinerator, the intermediate products should be transformed by two reactions, cracking and addition reactions. The cracking reaction occurred dominantly at 500–700 °C in the second-stage incinerator. When the incineration temperature was greater than 1200 °C, the addition reaction occurred dominantly and the major products were soots which are more thermally stable.

The analysis results in the 14 PAHs, as shown in Fig. 2, indicated that the critical temperature for the maximum yield of 14 PAHs was shifted from 1000 °C to 900 °C, when metallic chloride (BaCl₂ or NaCl) was added to the incineration system. The yields of 14 PAHs and soots were more with BaCl₂ or NaCl additive than those without metallic chloride additives. This indicated that metallic chloride additives could promote the reaction sequence towards the growth and coagulation reaction of soots from PS pyrolysis. When the second-stage temperature increased to the critical temperature, black tar formed and the concentration of 14 PAHs was 10⁴–10⁵ µg/g PS. Pha, Flu and Pyr were major species found among the 14 PAHs, as shown in Fig. 3. When the stage-two temperature was increased, the concentration of the 14 PAHs formed was decreased. The reason was that the thermal temperature provided enough energy for the low-ring PAHs to grow to high-ring PAHs and soot particulates. At incineration temperature above 1000 °C, the soot particulates of black powder formed and the weight of soot particulates formed increased as the stage-two pyrolysis temperature increased.

The above results also indicated that PAHs would effectively react with phenyl, biphenyl, naphthyl, binaphthyl, and C₂H₂ and grew to larger PAHs when the pyrolysis temperature was increased to a higher temperature of 1000 °C. Reactions of soot formation such as nucleation, condensation coagulation, aggregation mechanisms

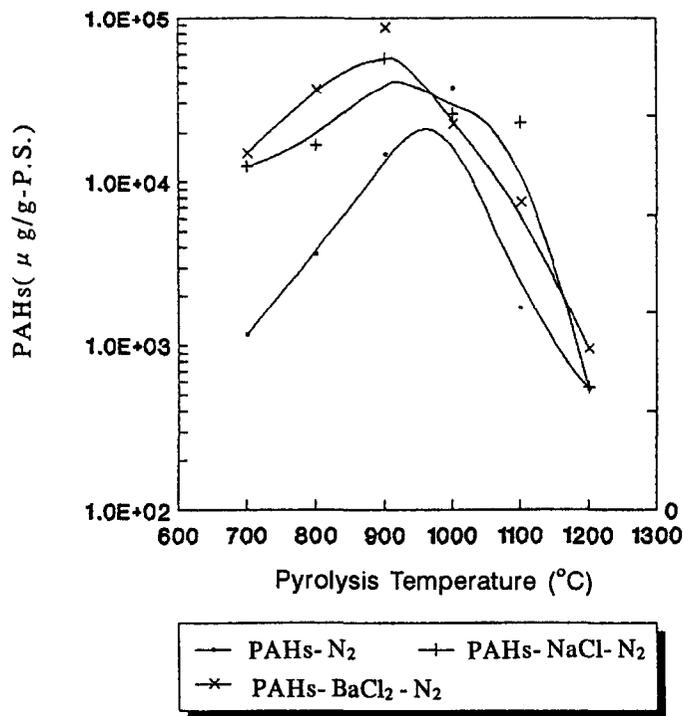


Fig. 2. Formation of 14 PAHs from polystyrene incineration with or without metallic chloride additives under various pyrolysis temperatures.

occurred effectively. Since the change in free energies caused by the series reactions of PAHs and soot formation was so large, reactions became practically irreversible. This, in turn, had the effect “of pulling” the reaction sequence forward towards formation of larger PAHs and soot particles. It has been postulated that mechanism for coagulation is through the reactions of aryl radical + PAH, and molecule and soot active site + soot [10].

Of the 14 species of PAHs, only Pha, Flu and Pyr were always found to be in the gas phase in the PUF sample. The reason may be that the boiling points and vapor pressures were low. The various distributions of 14 PAHs between the gas and solid phases resulting from the polystyrene incineration with or without metallic chloride additives were caused by various temperatures and oxygen supplies. The Pha, Flu and Pyr distributions between the solid and gas phases at various pyrolysis temperatures are shown in Fig. 4 and the relationship can be expressed as

$$\log K = -A/T + B,$$

where $K = \text{PAH}_{(\text{gas})}/(\text{PAH}_{(\text{solid})}/\text{particulates})$, T is the temperature of the second-stage incinerator (K) and A , B are constants.

Log K values, the ratios between the PAHs in gas phase and the PAHs in solid phases (per particulates weight; 1/mg) increased as the stage-two pyrolysis

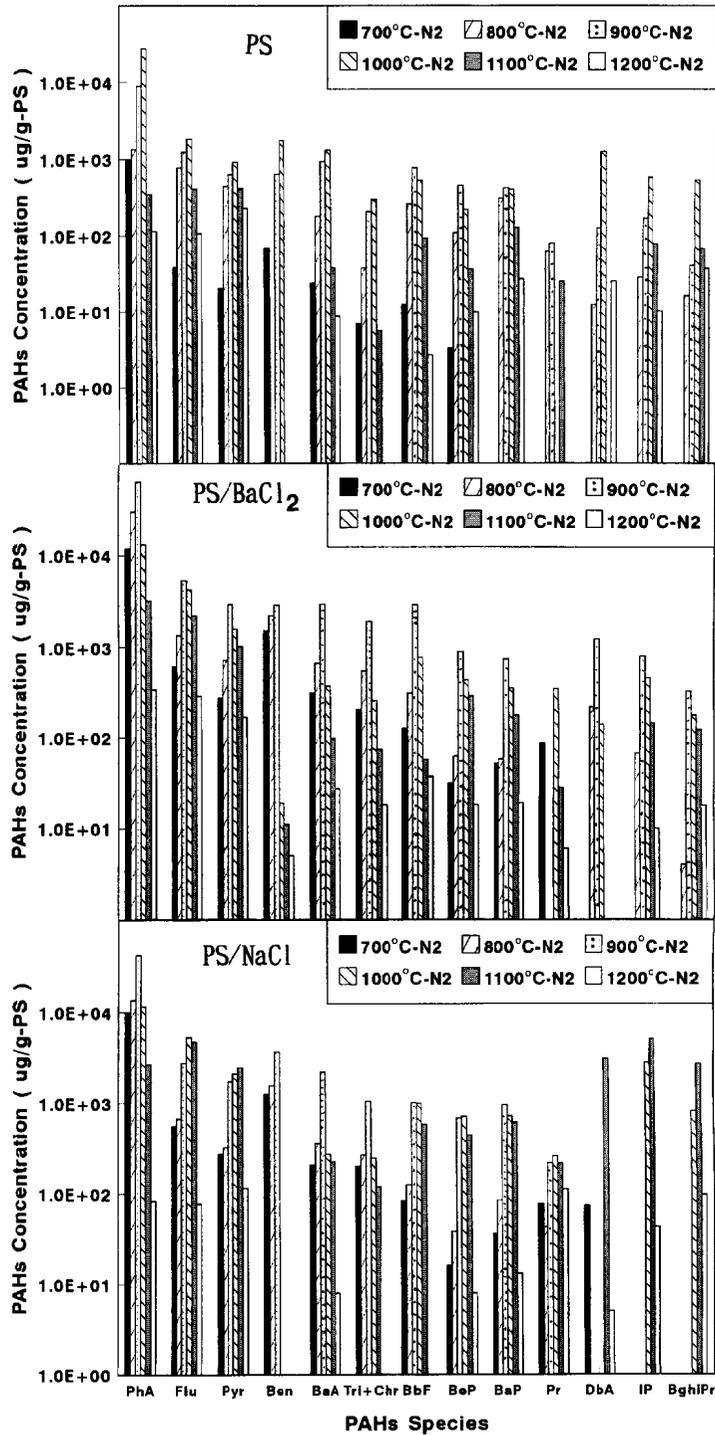


Fig. 3. Formation of 14 PAHs species during polystyrene incineration under various metallic chloride additives and various pyrolysis temperatures.

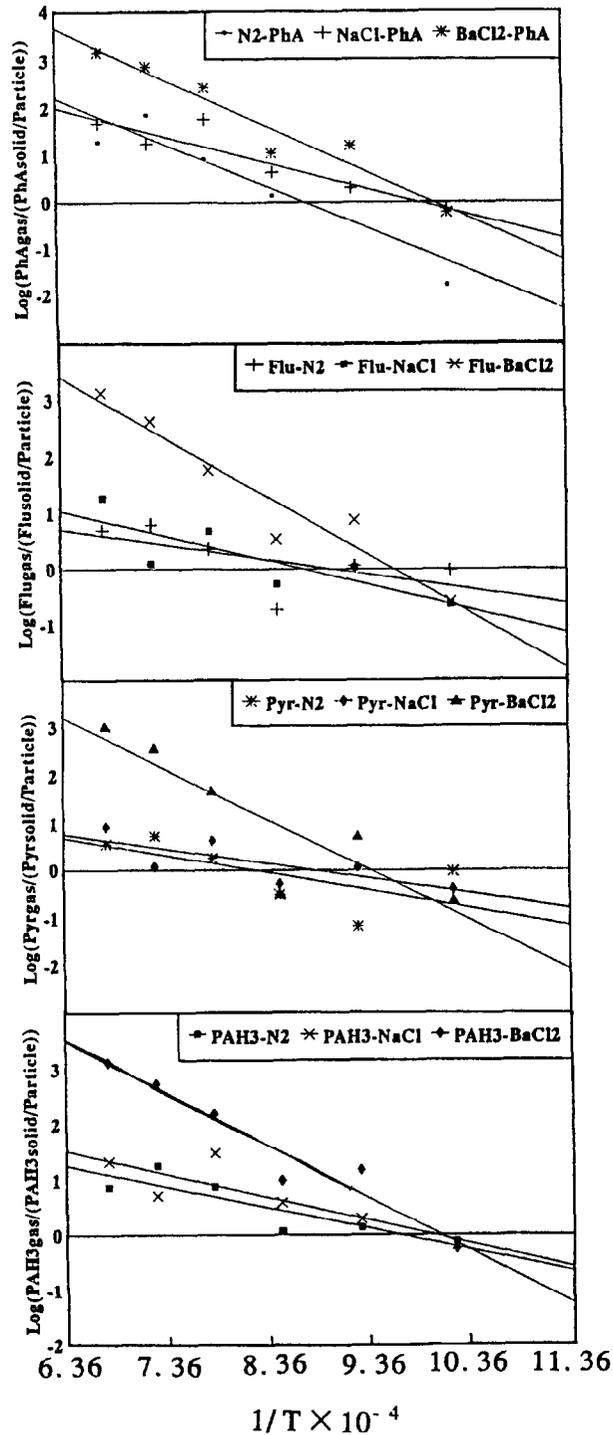


Fig. 4. The PAHs distributions between the solid and gas phases in air emissions from polystyrene incineration at various pyrolysis temperatures.

Table 3
The distribution constants of PhA, Flu, and Pyr between the gas and solid phases

Materials	Species	<i>A</i>	<i>B</i>	<i>R</i> ²
PS	PhA	8882.5	7.9	0.836
	Flu	2604.4	2.4	0.371
	Pyr	3612.3	3.0	0.471
	PAH ₃	3760.6	3.7	0.770
PS + BaCl ₂	PhA	9658.8	9.8	0.939
	Flu	10 211.2	9.9	0.992
	Pyr	10 372.7	9.8	0.771
	PAH ₃	9330.2	9.5	0.942
PS + NaCl	PhA	5523.3	5.5	0.854
	Flu	4294.8	3.8	0.669
	Pyr	3077.5	2.7	0.590
	PAH ₃	4135.8	4.2	0.737

Note: (1) $\log K = -A/T + B$; $K = \text{PAH}_{(\text{gas})}/(\text{PAH}_{(\text{solid})}/\text{particulates})$.

(2) $\text{PAH}_3 = \text{PhA} + \text{Flu} + \text{Pyr}$.

(3) *R*², correlation coefficient.

temperature increased. When the stage-two incineration system was controlled at 900 °C as were various oxygen supplies, the maximum value of $\log K$ occurred at 0.0525 O₂ (nl/min) and $\log K$ value decreased as the oxygen supply increased, as shown in Fig. 5 and the constants *A* and *B* are given in Table 3.

From the results of the TA98 Ames test in Table 4, when PS was pyrolyzed from 700 °C to 1200 °C, the mutagenicity was increased as the second-stage temperature increased, as shown in Fig. 6. The maximum mutagenicity of particulates extracts occurred at 1100 °C and were about 3000 revs/plate with BaCl₂ and NaCl additives. When the second-stage temperature increased to 1200 °C, the mutagenicity of the extracts decreased.

The mutagenicity of particulates and PUF extracts at the second-stage temperature of 900 °C and various oxygen supplies are given in Table 5. When oxygen supply was increased from 0 to 0.210 nl/min, the mutagenicity of particulates extracts from the PS incineration with metallic chloride additives was still more stronger. These results were surprising and they were very different from the previous results from the incineration of polystyrene without metallic chloride additives [19]. Also, the correlations between mutagenicity and PAH₇ (BaP, BbF, BaA, IP, DbA, Tri and Chr) from polystyrene incineration with BaCl₂ or NaCl additive at various operation conditions were not so good. The reason is that other toxic compounds (i.e., nitro-PAHs, dioxin and furan) might be formed and should be identified in future research work.

However, the mutagenicity of particulates and PUF extracts caused significantly higher potency of revertants to *S. typhimurium* TA98 in the presence of S9 mixture than that without S9 additive. This indicates that the emitted gas from the PS incineration contains not only direct-acting mutagens but also indirect mutagens, which

Table 4
Comparison of the mutagenicity of particulates and PUF extracts from polystyrene incineration under various stage-two pyrolysis temperatures (mutagenicity unit: revs/plate)

	700 °C		800 °C		900 °C		1000 °C		1100 °C		1200 °C	
	S9(+)	S9(-)	S9(+)	S9(-)	S9(+)	S9(-)	S9(+)	S9(-)	S9(+)	S9(-)	S9(+)	S9(-)
PS												
S	156	22	568	35	382	40	1626	226	2034	137	2178	72
G	30	55	45	22	50	31	154	66	100	64	60	54
PS + BaCl ₂												
S	226	181	689	458	279	121	649	98	3312	184	1070	108
G	61	35	74	20	47	18	203	39	1404	194	441	32
PS + NaCl												
S	249	126	325	148	438	290	891	192	2984	213	2188	106
G	53	30	78	40	75	26	74	40	58	57	63	23

Note: (1) S9(+): 0.1 ml sample with S9 additive; S9(-): 0.1 ml sample without S9 additive.

(2) S: solid phase (particulates extracts); G: gas phase (PUF extracts).

(3) The number of spontaneous revertants: S9(+), 30-40; S9(-), 27-38.

(4) A positive mutagenic response was defined as a dose giving at least 2-fold increase in revertant colonies per plate as compared with spontaneous reversion.

Table 5

Comparison of the mutagenicity of particulates and PUF extracts from polystyrene incineration under various oxygen supplies (mutagenicity unit: revs/plate)

	0 nl/min		0.0525 nl/min		0.105 nl/min		0.210 nl/min	
	S9(+)	S9(-)	S9(+)	S9(-)	S9(+)	S9(-)	S9(+)	S9(-)
PS								
S	382	40	520	155	123	59	93	58
G	50	31	125	60	95	57	94	24
PS + BaCl ₂								
S	279	121	636	207	254	107	1910	184
G	47	18	72	31	76	26	129	36
PS + NaCl								
S	438	257	344	322	691	377	527	70
G	75	26	49	22	82	48	39	28

Note: Same as Table 3.

are usually activated by the mixed-function oxygenases in the microsomes of animal liver to become ultimate mutagens whether the PS incineration system added metallic chloride or not. The mechanisms of epoxide formation and nucleophilic epoxide opening could be involved in metabolic oxidation. In the body, the epoxide ring should react with an amino group in cellular DNA to give an altered DNA that is covalently bound to the PAH. With its DNA thus altered, the cell was unable to reproduce normally. From the recent experimental results, sister chromatid exchanges in human lymphocytes were induced by the particulates extracts from polystyrene incineration, as shown in Fig. 7.

4. Conclusions

The critical temperature in the second-stage incinerator for the maximum yield of 14 PAHs was shifted from 1000 °C to 900 °C when metallic chloride (BaCl₂ or NaCl) was added to the incineration system. Log *K* values, the ratios between the PAHs in gas phase and the PAHs in solid phases (per particulates weight; l/mg) increased as the stage-two pyrolysis temperature increased. When the second-stage furnace was controlled at 900 °C and various oxygen supplies, the maximum value of log *K* occurred at 0.0525 O₂ (nl/min).

Concerning the mutagenicity in the air emissions, the maximum mutagenicity of particulates and PUF extracts occurred at 1100 °C, when the pyrolysis temperature was increased from 700 °C to 1200 °C. The mutagenicity of PUF extracts was weaker than the mutagenicity of particulates extracts. When oxygen supply was increased to 0.210 nl/min and stage-two temperature was controlled at 900 °C, the mutagenicity of particulates and PUF extracts were still higher for NaCl additive and were much higher for BaCl₂ additive. Moreover, the mutagenicity is much higher in the presence of rat liver microsomal fraction (S9 mixture) than that without S9 additive.

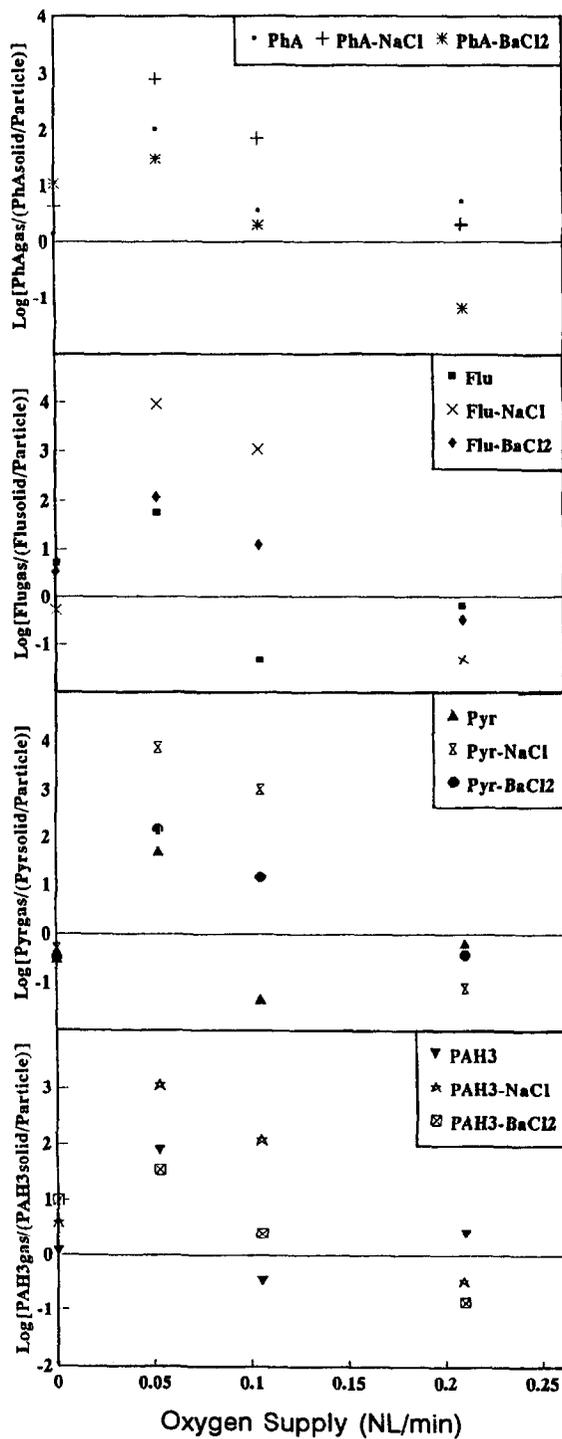


Fig. 5. The PAHs distributions between the solid and gas phases in air emissions from polystyrene incineration at 900 °C and various oxygen supplies.

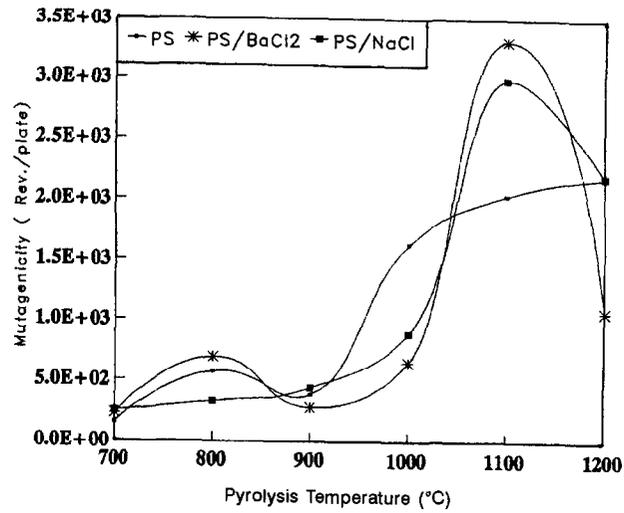


Fig. 6. The mutagenicity in air emissions from polystyrene incineration under various operation conditions.

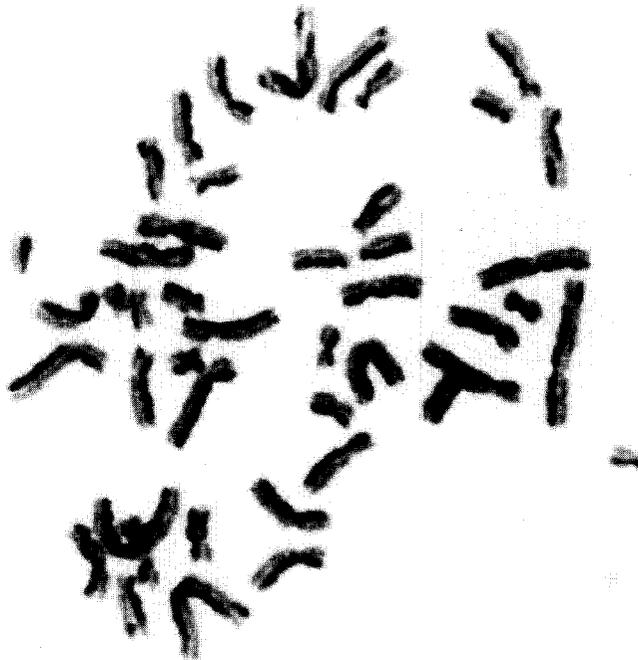


Fig. 7. Sister chromatid exchanges in human lymphocytes were induced by the particulates extracts from polystyrene incineration.

Finally, from the results of this study, the metallic chloride in the municipal solid waste (MSW) should be considered as an important factor in design and operation of MSW incinerator. As for the toxic control and the risk assessment of human health, the SCE (sister chromatid exchange) test in the air emissions from various incineration conditions should also be taken into consideration and this should be worth researching in the future.

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