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- Abstract -

A Study on exposure assessment of Coke-Oven Workers to Coke Oven Emissions and Polynuclear Aromatic Hydrocarbons

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Coke-oven workers are regularly exposed to coke oven emissions(COE), which consist primarily of polynuclear aromatic hydrocarbons (PAH) and volatile organic components. This study assessed the exposure of coke-oven workers to COE and PAH. The results of this study are as follows.

1. Among the 136 samples on coke-oven workers 33.1% exceeded the occupational exposure limit to the Coal Tar Pitch Volatiles(0.2 mg/m^3) established by the Korean Ministry of Labor and American Conference of Governmental Industrial Hygienists(ACGIH).
2. The coke-oven workers were classified into twelve job categories and there was statistically significant difference among the airborne concentrations of COE and PAH in twelve job

categories($p < 0.001$).

3. There was no significant difference of the airborne concentrations of COE between NIOSH method and OSHA method applied.
4. There was a significant correlation between the airborne concentrations of total PAH and COE($r=0.733$, $p < 0.01$).
5. The percentage of naphthalene in total PAH was 55.9% and the highest among those of 16 PAHs. There was a significant correlation between the airborne concentrations of naphthalene and total PAH($r=0.90$, $p < 0.01$) and this study recommends naphthalene as the index component of PAH.

Key Words : Coke-oven, COE, PAH

† : 2000 4 19 , : 2000 9 21
 : 7-3

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method)	.)	1Mℓ	(vacuum dry
P	1 , 2 , 3 , 4	oven)	40 , 50 200 mmHg	2
5	K P			30
(personal sample)				10-5g 가
8	.	METTLER TOLEDO	AG245	.
		COE		20
(calibration)	(field blank)			
	11.7			
20.7 ,	2.2 8.0 m/sec .	1		.
1. COE		2) OSHA	(OSHA, 1991)	
	(COE)	Glass fiber filter(binder free, 1μm, 37		
NIOSH	OSHA	mm,) Silver membrane filter(0.8μm, 37mm,)		
	COE	3-piece cassette	NIOSH	
가	가			
		2. PAH	(NIOSH, 1994)	
1) NIOSH	(NIOSH, 1994)	NIOSH	COE	PAH
	PTFE membrane filter(2μm, 37mm)			PTFE membrane filter
	PTFE membrane filter 3-piece	XAD-2 tube(100mg/50mg)		
cassette	UV PAH	XAD-2 tube		UV
	(NIOSH,			
1994).		2 LPM		(Gillian,
2 LPM	(Gillian,	U.S.A.)		
U.S.A.)				
		XAD-2 tube		
PTFE filter	(UV)	toluene 5 Mℓ	가	30
		syringe filter(0.45 μm, Millex-SR 25 mm		
PTFE filter가	methylene chloride	Millipore Co.)		
5 Mℓ 가		PTFE filter	XAD-2 tube	
30	COE	syringe filter(0.45 μm, Millex-SR 25 mm Millipore		
	syringe filter(0.45 μm, Millex-SR 25 mm	Co.)		(FID)가
Millipore Co.)		Gas Chromatography (Hewlett Packard HP- 6890		
(가 60mg	Plus)	1	.

Table 1. Systems and operating conditions for quantitative analysis of PAHs by GC

Variable	Condition
Systems	
Gas Chromatography	Hewlett Packard 6890 Plus
Detector	FID(Flame Ionization Detector)
Capillary Column	HP-5 MS(30m×0.32mm×0.25 μ m)
Carrier gas	N ₂ 1.5 ml/min
Operating Conditions	
Injection Mode	Split(20:1)
Injector Temperature	300 °C
Detector Temperature	320 °C
Oven Temperature Programming	75 to 280 °C

분석내용은 미국 환경보호청(Environmental Protection Agency, EPA)에서 PAH에 의한 대기오염의 지표로 설정하고 있는 16가지 PAH, *napthalene*, *acenaphthylene*, *acenaphthene*, *chrysene*, *anthracene*, *benzo(a)pyrene*, *pyrene*, *phenanthrene*, *fluoranthene*, *fluorene*, *benzo(b)fluoranthene*, *benzo(k)fluoranthene*, *benzo(ghi)perylene*, *benzo(a)anthracene*, *dibenzo(a,h)anthracene*, *indeno(1,2,3-cd)pyrene*에 대해서 정량분석을 실시하였다.

PTFE filter의 정량값에 회수율 및 공시료 값을 적용하였으며 XAD-2 tube의 정량값에 탈착효율 및 공시료의 값을 적용하였다.

PTFE filter와 XAD-2 tube로부터 PAH 각각의 노출수준 및 16가지 PAH 노출수준을 합한 total PAH 노출수준을 산출하였으며 실작업시간동안의 노출수준을 8시간 시간가중평균 노출수준(Time Weighted Average, TWA)으로 환산하여 결과를 산출하였다.

III. 연구결과 및 고찰

1999년 10월 15일~11월 10까지 코크스로를 관리

하는 협력업체 작업자에 대한 COE와 PAH 노출수준을 평가한 결과는 다음과 같다.

1. 평가일별 COE 및 PAH 노출수준

본 연구에서 실시한 코크스로 1기, 2기, 3기, 4기, 5기 작업자들에 대한 COE와 PAH의 평가일별 노출수준 결과를 요약하면 표 2와 같다.

평가일별로 COE 측정 및 분석방법(NIOSH 방법, OSHA 방법)을 달리하였으며 PAH는 NIOSH 방법으로 노출수준을 평가하였다. 각 노출수준 결과는 개인시료(Personal sample) 결과를 토대로 한 것이다.

평가기간동안 코크سوب본작업자들의 COE의 노출수준은 기하평균이 0.31 mg/m³, 범위가 <0.01~ 2.24 mg/m³으로 나타났다.

산업위생 통계학자인 Leidel 등(1977)은 NIOSH 연구자료를 토대로 분석하여 공기중 유해물질 수준에서 단시간 측정치는 일반적으로 대수정규분포를 하고 있으며 기하표준편차(GSD)는 1.5~2.0이라고 발표하였다. COE 노출수준의 경우 기하표준편차가 비교적 높은 것으로 나타났으며 이는 COE 노출수준이 작업조건에 따라 변이가 심하다는 것을 말해준다. 따라서 정확한 평가를 위해서는 작업조건을 고려한 반

Table 2. Comparison of airborne concentrations of COE and PAHs by sampling days

	COE (mg/m ³)					total PAHs (μg/m ³)			
	GM*	GSD †	Range		Violation(%) ‡	GM*	GSD †	Range	
K company									
October 15 (NIOSH method)	0.34 (N §=29)	3.59	<0.01	2.24	31.0 % (9/29)	36.66	1.52	17.25	96.41
November 1 (OSHA method)	0.33 (N §=30)	4.39	<0.01	1.25	46.7 % (14/30)				
November 2 (NIOSH method)	0.29 (N §=26)	4.78	<0.01	2.17	38.5 % (10/26)				
S company									
November 9 (NIOSH method)	0.27 (N §=24)	3.66	<0.01	1.36	37.5 % (9/24)	32.05	1.54	15.59	76.90
November 10 (OSHA method)	0.32 (N §=27)	3.46	<0.01	1.36	44.4 % (12/27)				
TOTAL	0.31	3.86	<0.01	2.24	33.1 % (45/136)	34.37	1.53	15.59	96.41

* : Geometric Mean
† : Geometric Standard Deviation
‡ : Violation percentage of COE exposure limit(0.2 mg/m³), %
§ : Number of samples

가 (ANOVA) NIOSH
COE OSHA 가
(Coal Tar (p>0.1).
0.2 mg/ COE
Pitch Volatiles, 가)
m³ COE 가
, OSHA COE 2
0.15 mg/m³ COE
0.2 mg/m³ COE total PAH
136 45 (31.0%) 34.37 μg/m³, 15.59 96.41 μg
/m³ PAH 16가 total PAH
가 COE 가 (200 μg/m³)
(Analysis of variance, ANOVA)
가 (p>0.1).
COE COE 가

167 μ g/m³ naphthalene 10 ppm(50 chrysene PAH (r) 0.733 (p<0.01). COE
 benzo(a)pyrene PAH = 32.726 + 0.022COE
 가 (American Conference of COE PAH
 Governmental Industrial Hygienist, ACGIH - 53.73%
 ACGIH) (A2) (R²=0.5373, p<0.001).
 PAH
 3 OSHA, NIOSH, ACGIH 2. COE PAH
 PAH
 NIOSH COE
 total PAH COE (lidsman), (gooseneck
 PTFE filter 가 cleaning), (door sealing/stripping),
 total PAH PTFE filter XAD- 2 (battery side cleaning),
 PAH (mortar gunning of battery inside),
 PAH COE (mortar spraying of battery inside),
 Sealing(battery wall luterman),
 COE PAH carbon (door carbon remover), Sole flue
 (Sole flue maintenance), CDQ (,

Table 3. Exposure limits of PAHs

Compound	OSHA	NIOSH	ACGIH
naphthalene	10ppm, 50mg/m ³	10ppm, STEL 15ppm	10ppm, STEL 15ppm
acenaphthylene	-	-	-
acenaphthene	-	-	-
fluorene	-	-	-
phenanthrene	0.2mg/m ³	-	-
anthracene	0.2mg/m ³	-	-
fluoranthene	-	-	-
pyrene	-	-	-
benzo(a)anthracene	-	-	suspect carcinogen, A2
chrysene	0.2mg/m ³ (benzene sol.)	lowest feasible, carcinogen	suspect carcinogen, A3
benzo(b)fluoranthene	-	-	suspect carcinogen, A2
benzo(k)fluoranthene	-	-	-
benzo(a)pyrene	0.2mg/m ³ (benzene sol.)	0.1mg/m ³ (cyclohexane sol.)	suspect carcinogen, A2
dibenzo(a,h)anthracene	-	-	-
indeno(1,2,3- cd)pyrene	-	-	-
benzo(g,h,i)perylene	-	-	-

- CDQ cleaning), COE
 (gooseneck maker) (worker PAH 가
 manegement) (ANOVA) 가
 COE PAH 가 . (p<0.001). Mei- Lien Chen (1999)
 (operating room of larry car) , COE
 () (top side of the battery) . COE 가
 COE (Benzene soluble faction, BSF) .
 가 . COE PAH COE 가
 4 . COE
 0.8 mg/m³ .
 0.2 mg/m³ 50 cm

Table 4. Airborne concentrations of COE and PAHs by processes

PROCESS	COE (mg/m ³)					total PAHs (μg/m ³)			
	N*	range		GM †	Violation ‡	N*	range		GM †
lidsman	15	<0.01	1.27	0.31	33.3 % (5/15)	5	18.31	54.98	43.47
gooseneck cleaning	19	<0.01	1.36	0.18	31.6 % (6/19)	7	22.03	56.76	39.34
door sealing/stripping	39	<0.01	2.24	0.36	43.6 % (17/39)	12	20.42	96.41	37.65
battery side cleaning	8	<0.01	1.14	0.69	87.5 % (7/8)	4	29.12	44.11	33.22
mortar gunning of battery inside	3	0.17	0.58	0.3	66.7 % (2/3)	-	-	-	-
mortar spraying of battery inside	4	<0.01	0.86	0.80	75.0 % (3/4)	-	-	-	-
battery wall luterman	6	<0.01	0.02	-	-	3	22.63	39.70	27.54
door carbon remover	8	<0.01		-	-	-	-	-	-
Sole flue maintenance	14	<0.01	1.39	0.33	57.1 % (8/14)	8	15.59	57.11	34.20
CDQ cleaning	8	<0.01	0.64	0.24	12.5 % (1/8)	2	17.25	31.57	23.24
gooseneck maker	2	<0.01		-	-	-	-	-	-
worker manegement	5	<0.01	0.98	0.21	40.0 % (2/5)	2	23.65	41.98	31.51
operating room of larry car	10	<0.01	1.56	0.71	50.0 % (5/10)	4	34.35	73.17	51.42
larry car outside	6	<0.01	0.93	0.79	-	1	27.61		-
top side of the battery	9	0.41	5.51	1.25	-	2	77.42	175.67	116.62

* : Number of samples
 † : Geometric Mean
 ‡ : Violation percentage of COE exposure limit(0.2 mg/m³), %

가

가

가

가
(positive pressure)

0.3 mg/m³

COE가

Mei- Lien Chen (1999) COE

(lidmen) 0.52 mg/m³,

(tar chaser) 0.43 mg/m³,

(larry operator) 0.19 mg/m³

8 0.2 mg/

m³ 가 7 87.5% 가

COE

(door

sealing/stripping) COE 가

0.36 mg/m³ ()

(2.24 mg/m³) 가

가 1 4

COE(

가)가

0.79, 1.25 mg/m³

COE

COE

Sole flue (1) COE

가

가

가

COE가

COE

0.33 mg/m³

(HEPA filter)

COE

(0.31 mg/m³)

(0.18 mg/m³)

가

PAH

가

(0.71 mg/m³) COE PAH 43.47 µg/m³

COE PTFE filter emissions), 가 가
가 total PAH PTFE (pushing emissions)
filter XAD-2 PAH COE
가 .
(NIOSH, 1980).
가 가
PTFE filter XAD-2
PAH가 .
(,
Sole flue)
COE PAH .
가
COE
PAH (, , ,
) .
. (), ()
, , , , ,
, , , , 가 가
, 가
COE PAH
. 가
. COE가
OSHA
“ ”
(0.15 mg/m³)
, .
NIOSH COE , , , ,
, , (USA Depart-
ment of LABOR, 1990).
가
(side door leaks), 가 (1997)
(topside leaks), 가 (charging pyrene

1- OH- pyrene	56.3%	5	total PAH(PTFE filter + XAD- 2)
		PAH	total PAH
		100 %	PAH %
(가)		PTFE filter	XAD- 2 PAH
,		total PAH %	(1, 2
가)			
		total PAH	PAH
		naphthalene	total PAH 55.9%
3. total PAH			acenaphthylene, chry-
			sene
			indeno(1,2,3- cd)pyrene,
			dibenzo(a,h)anthracene, benzo(ghi)perylene
NIOSH Method	PAH		
가	PAH	PAH	total
	PAH	PAH(PTFE filter + XAD- 2 tube)	67.2% 가 XAD- 2

Table 5. Comparison of contents of PAHs by sampling media(unit : %)

	PTFE filter+XAD- 2 tube (N*=58)	PTFE filter (N*=58)	XAD- 2 tube (N*=58)
Naphthalene	55.9	12.0	43.9
Acenaphthylene	9.8	4.9	4.9
Acenaphthene	4.8	2.5	2.3
Fluorene	1.6	-	1.6
Phenanthrene	4.4	0.6	3.8
Anthracene	0.4	0.1	0.3
Fluoranthene	1.7	0.7	1.0
Pyrene	1.2	0.8	0.4
Benzo(a)anthracene	1.8	0.9	0.8
Chrysene	8.5	6.2	2.2
Benzo(b)fluoranthene	5.0	1.9	3.1
Benzo(k)fluoranthene	3.9	2.1	1.8
Benzo(a)pyrene	1.0	-	1.0
Indeno(1,2,3- cd)pyrene	-	-	-
Dibenzo(a,h)anthracene	-	-	-
Benzo(ghi)perylene	-	-	-
PAH	100	32.8	67.2

* : Number of samples

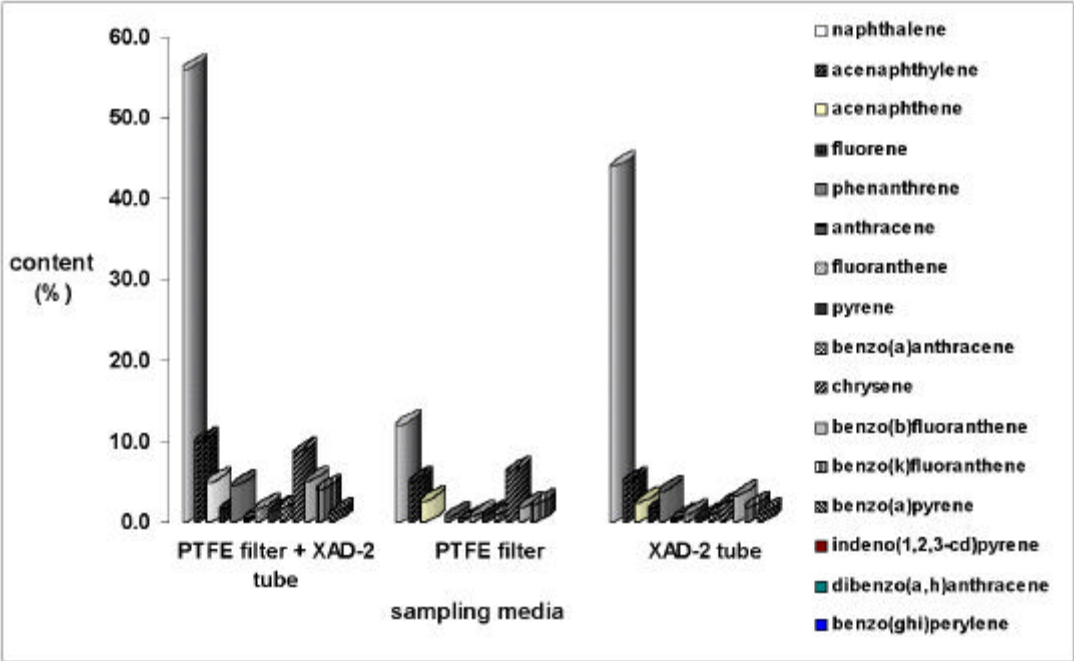


Figure 1. Comparison of contents of PAHs by sampling media

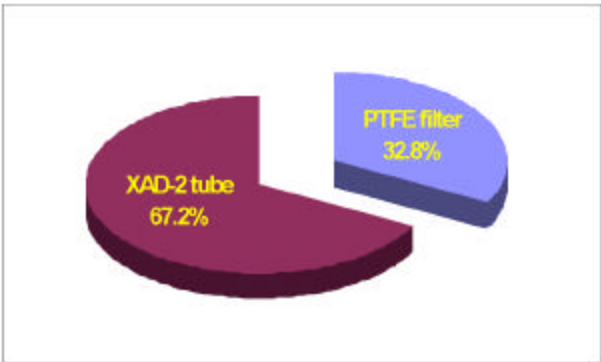


Figure 2. Comparison of contents of total PAHs by sampling media

NIOSH	COE	PTFE filter	PAH	COE
	COE	PAH		
가 PTFE filter		COE	가	16가 PAH
가 PTFE filter				naphthalene(C ₁₀ H ₈)
		XAD-2 tube		PAH (C ₆ H ₆)

가 2 6 PTFE filter total PAH(PFFE filter + XAD-2 tube) anthracene, naphthalene, phenanthrene, fluoranthene, fluorene, pyrene (P<0.05).

가 4 5 filter PAH가 XAD-2 PTFE (1993) pyrene, fluoranthene, phenanthrene, anthracene total PAH

3 가 PAH가 Farant (1998) pyrene, benzo(a)anthracene, benzo(a)pyrene total PAH

Erkki Yrjanheikki (1995) PAH(naphthalene, fluorene, phenanthrene) XAD-2 tube (a)pyrene total PAH

3 (1988 1990) naphthalene 8 500 $\mu\text{g}/\text{m}^3$, PAH pyrene

fluorene, phenanthrene 0.58 24.64, 0.16 (r=0.94).

18.76 naphthalene PAH PAH pyrene

benzo(a)pyrene pyrene

6 PAH total PAH anthracene

total PAH PAH total PAH 55.9 %

naphthalene

naphthalene PAH 가

Table 6. Relationship between total PAHs and each PAH

	Correlation Coefficient		
	Kwon et al.	Yoon and Paik(1993)	Farant and Manon(1998)
naphthalene	0.90	-	-
acenaphthylene	0.74	0.90	-
acenaphthene	0.23	0.62	-
fluorene	0.83	0.87	-
phenanthrene	0.89	0.94	-
anthracene	0.92	0.94	-
fluoranthene	0.87	0.96	-
pyrene	0.82	0.97	0.990
benzo(a)anthracene	0.64	-	0.992
chrysene	0.22	-	-
benzo(b)fluoranthene	0.26	0.89	-
benzo(k)fluoranthene	0.30	-	-
benzo(a)pyrene	-	0.93	0.951
indeno(1,2,3- cd)pyrene	-	0.71	-
dibenzo(a,h)anthracene	-	0.56	-
benzo(ghi)perylene	-	0.96	-

가 PAH 3 total PAH naphthalene
가

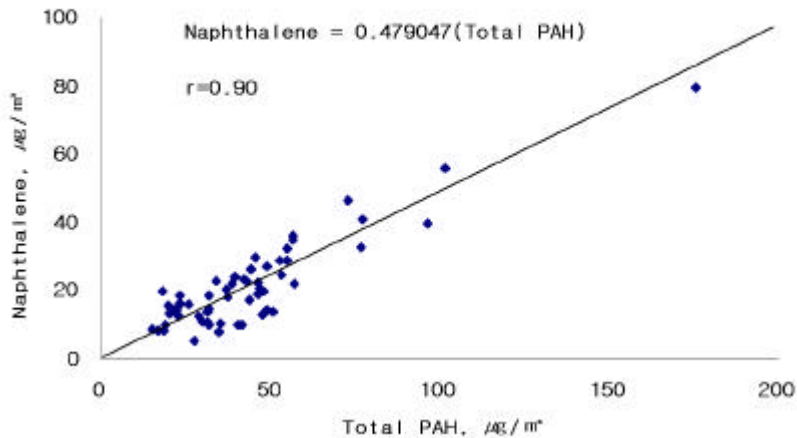


Figure 3. Relationship between naphthalene and total PAHs

(0.2 mg/m³)
COE (NIOSH OSHA
) COE 가
(p>0.1).
COE total PAH
0.733
(p<0.01).
COE PAH
가 (p<0.001). COE
가
0.2 mg/m³ COE
136 45 (33.1%)
total PAH
34.37 µg/m³, 15.59 96.41 µg/m³
COE
COE
, Door Sealing Strip Door
, Sole flue
COE
COE

0.31 mg/m³

PAH

가

PAH 43.47 µg/m³

total PAH 16가 PAH

naphthalene total PAH 55.9%

ancenaph-
thylene, chrysene . indeno-
(1,2,3- cd)pyrene, dibenzo(a,h)anthracene, benzo-
(ghi)perylene

PAH total

PAH(PTFE filter + XAD- 2 tube) 67.2% 가

XAD- 2

가 16가 PAH

naphthalene

total PAH PAH

total PAH anthracene, naph-
thalene, phenanthrene, fluoranthene, fluorene,
pyrene (P<0.05).

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가

; 1998

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1993;3(1):37- 53

1-

OH- pyrene PAH

가

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