DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM INCINERATION EMISSION SAMPLES

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Title of Thesis: DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM INCINERATION EMISSION SAMPLES

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ABSTRACT

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Robert Cebula, Master of Science, 1988

Thesis directed by: Professor of Chemistry,
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Stack emissions from five sources (one pulverized coal combustion operation, three sewage sludge incineration operations and one gray tin refractory operation) were sampled by use of U.S. EPA Modified Method 5 isokinetic sampling unit for vapor and particulate effluent. The sampling unit provided XAD-2 resin samples, polytetrafluoroethylene and glass fiber filters and impinger washings of dichloromethane. The resins were soxhlet extracted using dichloromethane (DCM) and the filters were soxhlet extracted using DCM followed by acetone. Fractionation of extracts was accomplished by thin layer chromatography. The resulting fractions were analyzed for polycyclic aromatic hydrocarbons (PAH), nitro-PAH and quinone-PAH by high-performance liquid chromatography (HPLC). Extractable organic matter (EOM) was also determined with a electrobalance. XAD samples from a gray tin refractory, and three sewage sludge incinerators

higher molecular weight PAH. The volatility of the low MW PAH was responsible for the high concentration found in the resins. The lower boiling point of the higher MW PAH and the stronger association of high MW PAH with fly ash are reasons for their presence in the filter samples. No nitro-PAH or quinone-PAH compounds were detected in the emission samples. Of the four XAD resins analyzed for B(a)P by fluorescence scanning three samples showed very similar results. Concentrations from the three sources resulted from two different operations. Comparison of the HPLC results for B(a)P and fluorescence scanning of selected XAD resins have not resulted in good agreement. Phthalates tend to interfere with the HPLC chromatogram in the area where B(a)P elutes. This most likely is the reason for the disagreement. Tetrachloro-p-dibenzodioxin was observed in the resin and washings of the Parsippany Troy Hills source (sewer sludge incinerator). Heptachloro-p-dibenzodioxin was observed in the filter samples of the PSE&G source (coal combustion). The higher chlorinated species seem to form a stronger association with the particulate and a weaker association with the lower chlorinated species.

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I. PROJECT INTRODUCTION

The purpose of this project has been to determine the presence of various polycyclic aromatic hydrocarbons (PAH), selected derivatives and chlorinated dibenzo-p-dioxins and dibenzofurans in stack emissions from waste incineration facilities. Polycyclic Aromatic Hydrocarbons have been the subject of many studies because many are carcinogenic and/or mutagenic. The primary goal of the present project is quantitation and comparison between different sources. The samples for this project were obtained from five incineration sources. The United States Environmental Protection Agency (EPA) Modified Method 5 was employed for sample collection. The key feature of this procedure is the addition of a sorbent trap used to collect the vapor phase effluent. The samples were analyzed by High Performance Liquid Chromatography (HPLC). The Method 5 sampling train consisted of three sampling parts (XAD-2 sorbent, filter and washings from impinger and train rinse) (Appendix fig #1). Samples for HPLC analysis were fractionated by Thin Layer Chromatography (TLC) [1]. The TLC plated were sectioned into three fraction areas (PAH, nitro-PAH and quinone). A limited number of XAD-2 resin samples were analyzed for benzo (a)pyrene by a plate scanning spectrofluorometer. Also a limited number of sample portions were sent to an outside testing laboratory (ETC,Edison, N.J.) for analysis of a series of chlorinated dibenzo-p-dioxins and dibenzofurans.

II. EXPERIMENTAL SECTION

A. XAD-2 SORBENT SAMPLE PREPARATION

The XAD-2 (amberlite) resins were removed from their holding traps. The total mass of the resin was determined with an analytical balance. Twenty-five percent of the mass of each sample run was reserved for optional dioxin/furan analysis. The remaining resin mass was placed into a soxhlet thimble which in turn was placed into a soxhlet apparatus. The resins were extracted using 200 ml dichloromethane (DCM) for 24 hours. The resulting extract was rotoevaporated under vacuum and heat, concentrated to 10 ml with a stream of nitrogen (99.998%), clarified with a 10 ml syringe connected to a filter unit (MILLEX-SR 0.5 micron) and stored at -15 C.

B. FILTER SAMPLE PREPARATION

The filters (125 mm dia.) received were of two types: polytetrafluoroethylene (PTFE) from the Parsippany and Pequannock sources and glass fiber from the PSE&G, Wayne, and Griffin Pipe sources. The filters were cut in half. Half was reserved for optional dioxin/furan analysis. The filters were then placed into a soxhlet thimble and assembled into a soxhlet apparatus. The filters were first extracted with 200 ml dichloromethane for 24 hours. The resulting extracts were then roto-evaporated, concentrated to 10 ml with nitrogen, clarified and stored at -15 C. The apparatus was reassembled for a second extraction with 200 ml acetone for 24 hours. These acetone extracts were roto-evaporated, clarified, and concentrated to 10 ml with nitrogen and stored.

C. THIN LAYER CHROMATOGRAPHY (TLC) FRACTIONATION

The dichloromethane sample extracts obtained from the sampling train (XAD resins, filters, washings) were solvent exchanged to cyclohexane using roto-evaporation and nitrogen blowdown. The resulting samples were spotted on 20 x 20 cm precoated silica plates (Analabs - Anasil GF-250 micron layer). The spotting was done on an automatic spotter (AES model) with temperature and speed controls (settings: temperature 5, speed 1). In addition to the sample extracts, PAH, nitro-PAH and quinone standards were spotted in adjacent channels on each TLC plate. The plates were allowed to dry in the dark and then developed in the dark with a 1:1 solution of n-hexane and toluene. After drying, the plates were examined with a hand-held ultra-violet (UV) lamp. The standards help to identify the fraction areas. Three were areas selected for fractionation (PAH, nitro-PAH, quinone). These separate areas were scraped from the plates. The PAH scraping was placed into a thin pyrex tube with a fritted bottom (ASTM 40-60 C). The PAH fraction was then extracted from the scraped silica powder by adding 6 ml of tetrahydrofuran (THF) to the tube. The nitro-PAH and quinone scrapings were placed into 25 ml vials. Methanol was added to the vials. The vials were then sonicated (Sonic System, Inc. Model E5C4, Newtown, PA) at the boiling point of Methanol (68 C) for 20 minutes. The fractions were then clarified and stored.

D. SAMPLE PREPARATION FOR WASHINGS OF SAMPLING TRAIN

The front and back washings consisted of impinger and train rinses. The solvents employed were methyl alcohol and dichloromethane. These front and back solutions were mixed, The volumes of the mixed washings were determined and half of each was reserved for optional dioxin/furan analysis. The remaining portion was clarified and roto-evaporated to 5 ml. The sample was then solvent exchanged to cyclohexane and concentrated to 1 ml by a stream of nitrogen. The samples were then fractionated on a 20 X 20 cm TLC plate (Silica gel type, 250 micron layer, Anasil-GF, Analabs, North Haven, CT). These washings contained large quantities of particulate matter and thus required numerous clarifications.

E. DETERMINATION OF EXTRACTABLE ORGANIC MATTER (EOM)

Fifty (50) microliter volumes of the XAD resin extracts and filter extracts were placed on a pan. The mass of the pan was predetermined. The extract solvent was evaporated on a slide warmer at 40 C. The pans were then placed on a Cahn (model #26) electro-balance for sample EOM determination. This procedure was used for XAD extracts which were in dichloromethane and for filter extracts which were in dichloromethane as well as acetone. The EOM results are presented in Tables I and II. In Table I, the XAD extract results are presented the largest average value are observed in the Parsippany Troy Hills XAD samples. The lowest average values were observed in the Pequannock Lincoln Park samples; the low average was associated with the lowest standard deviation. Similarly the Griffin Pipe samples resulted in the second lowest average and second lowest standard deviation. In Table II, the filter EOM values for dichloromethane (DCM) and acetone extracts are presented. Of the DCM extracts the Wayne source had the largest values and the largest standard deviation. Of the acetone extracts the Wayne source resulted in the highest EOM value with a relativly low standard deviation. It difficult to observed any particular pattern in these results, but the Griffin Pipe source does shows almost exact average EOM values for XAD extracts, acetone filter extracts and DCM filter extracts.

F. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) UNIT AND ANALYSIS

The HPLC unit used for PAH, nitro-PAH and quinone detection and quantitation was a Waters Associates Inc. model. The system included a solvent programmer (model 660), two dual constant driven positive-displacement pumps (model 6000A), dual beam absorbance detector (model 440) and a fluorescence detector (model 420AC). The HPLC column used in this project was a VYDAC (Hesperia, CA) reverse phase C18 bonded column (#201TP54). The column was maintained at 15 C by a temperature jacket controlling unit.

F.1. PAH ANALYSIS BY HPLC

The gradient used for this analysis started at 35% acetonitrile/water and ended at 100% acetonitrile in 35 minutes with a linear change in concentration and the concentration was maintained at 100% for approximatly 15 minutes to elute all NBS 1647 compounds. The water was prepared by pumping distilled water through a series of filters (Millipore; Milli-Q Waters System model ZD 20 115 84). The filters remove organic and bacterial contaminants and deionize the water. The column was operated at 15 C. The standard used in this analysis was National Bureau of Standards reference material 1647 (NBS 1647). The standard includes sixteen polycyclic aromatic hydrocarbons in solution. Three detectors were used to determine the presence of these compounds. This included two UV absorption detectors at wavelengths: 280 nm and 365 nm. In addition, a fluorescence detector was used (excitation 360 nm. : emission > 440 nm). The presence of an unknown peak (possibly a water soluble impurity) in the area of the 280 nm signal for anthracene and phenanthrene restricted detection of these two PAH's which were determined by the 365 nm and fluorescence signals.

The NBS standard was injected into the system at various volumes. The signal areas were then related by regression analysis providing a calibration curve. In addition, detector ratios were determined in order to compared them to standards. This is a valuable indicator in determining the presence of a compound because retention time is not the sole indicator since different compounds often coelute.

F.2. HPLC NITRO-PAH ANALYSIS

The HPLC unit set-up for PAH is changed for nitro-PAH analysis. A reducer column is placed at the outlet of the UV absorbance detector. Since nitro-PAH are not strong fluorescing compounds they are reduced to amines by the reducer column which contains 1:1 zinc/silica with the aqueous part of the solvent at PH 3.4. The reduction occurs just prior to the inlet to the fluorescence detector. This reduction results in strongly fluorescing compounds. The set-up for the quinone-PAH and the nitro-PAH were the same.

G. RESULTS OF GC/MS ANALYSIS OF SELECTED XAD EXTRACTS

Selected samples of dichloromethane extracts of XAD resins were sent to Drs. Robert Rosen and Thomas Hartman of the Center for Advanced Food Technology of Cook College of Rutgers University for GC/MS analysis. The GC conditions included hot on-column injection (290 C) into a 15 meter DB-5 column (.25 mm ID, 0.25 um film thickness) (J&W Scientific). The temperature program started at 100 C for 3 minutes and then up to 320 C at 4 C/minute.

The following results represent a listing of positive identifications.

Public Service Electric and Gas XAD Sample

(Operation: pulverized coal generating station)

The positive identifications included the following compounds:

Molecular Weight	Name (class)
222	diethyl phthalate
262,272	other phthalates
284	stearic acid
300	dehydroabietic acid (sesquiterpene derivative)
314	methyl dehydroabietic acid (sesquiterpene)
326	steroid
408	aliphatic hydrocarbon
454	steroid
470	steroid
415	steroid
430	steroid
540	steroid

Parsippany/Troy Hills XAD Resin/ DCM Extracts
(Operation: municipal sewage sludge incineration)
In order of Elution:

MAJOR COMPOUNDS
xylenes
benzaldehyde
phenyl isocyanide
2,3-dihydroxy-2-(1-methylethyl) butanoic acid
2-nitrophenol
a dimethylbenzaldehyde isomer (not 2,5-)
a dimethylacetophenone isomer
naphthalene
benzoic acid
a methylnaphthalene
biphenyl
dimethylnaphthalenes
dimethylbenzoic or ethylbenzoic acid
a methylbiphenyl
dibenzofuran
dibutylphthalate
palmitic acid
di(ethylhexyl)phthalate

MINOR COMPOUNDS
trimethylbenzene(s)
fluorenone
phenanthrene or methylenefluorene
a phenylnapthalene
a methyl naphthalene or phenylindene
various phthalates
pyrene
fluoranthene
2,3,5-trimethylphenanthrene
stearic acid
several steroids
docosanoic acid
stigmast-5-en-3-ol

Pequannock Lincoln Park
(Operation: municipal sewage sludge incineration)
COMPOUNDS

a dimethylbenzaldehyde isomer

a dimethyl or ethylbenzaldehyde isomer

2-methylbenzofuran

benzoic acid

2,4-dimethylacetophenone

a demethoxyacetophenone

tetramethylphenol (?)

organophosphate (sample 539-555) esp. m/e 99
(tributylphosphate ?)

diethylphthalate

a sesquiterpene

palmitic acid

hexadecanoic acid

dioctylphthalate

other phthalates

H. BENZO(a)PYRENE ANALYSIS BY FLUORESCENCE SPECTROPHOTOMETER

Four XAD extracts have been examined for B(a)P with the Perkin Elmer plate scanning Fluorescence Spectrophotometer using an excitation of 387.0 nm and emission of 428.6 nm. The samples consisted of one run each from four sources.

1.) Parsippany Troy Hills (run #2)
2.) Pequannock Lincoln Park (run #2)
3.) Wayne Twp. Sewerage Authority (run #2)
4.) Griffin Pipe (run #3)

A four milliliter portion of each extract was spotted along with B(a)P standards on a 20% acetylated cellulose precoated TLC plate. The areas for spotting the samples consisted of channels. Eighteen channels were used: ten for standards (five concentrations in duplicate) and eight for samples. The peaks were examined for consistency with duplicate standard concentrations. The average peak area was then placed into a computer program. Since the values were very low, a linear relationship of signal to concentration of standards was assumed for these calculations rather than a quadratic relationship which is common for more widely varied fluoresence signals. The values are presented in Table III.

III. POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

A. PAH INTRODUCTION

Polycyclic Aromatic Hydrocarbons have been the subject of many studies because many of these compounds are carcinogenic. Some of these compounds have been specifically classified as initiators, carcinogens and complete carcinogens [2] in animal studies. Initiators such as benzo(e)pyrene and dibenz(a,c)anthracene and carcinogens such as pyrene and fluoranthene require promoters in order to induce benign or malignant tumors. Complete carcinogens such as benzo(a)pyrene and dibenz(a,h)anthracene do not require promoters for tumor induction to occur. Complex mixtures such as smoke or tar include promoters that lead to tumor induction [3]. A common feature associated with many of these PAH compounds is the requirement of activation. Specifically termed precarcinogens which are activation-dependent, this type of carcinogen, upon activation, results in the formation of an ultimate carcinogen. These ultimate carcinogens can then bind covalently to nucleic acids [4]. The activation-dependence is best described by the enzyme activation of benzo(a)pyrene (B(a)P). The cytochrome P-450 enzyme system used for metabolism can activate B(a)P by first epoxidation leading to the formation of a diol in the 7,8 position followed by further epoxidation in the 9,10 positions. The key carcinogenic product is the B(a)P-7,8-diol-9,10-epoxide. This type of activation has also been shown to occur with other PAH compounds [5]. Major sources of PAH compounds include combustion of coal, oil, gas and wood. Indoor wood heaters were found to significantly contribute to PAH concentrations [6]. PAH emissions from automobiles with spark ignition engines were shown to result in larger concentrations of anthracene, phenahthrene, fluoranthene, and pyrene relative to higher molecular weight PAH including benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(j)fluoranthene, benzo(a)pyrene, benzo(e)pyrene and indeno(1,2,3-cd)pyrene. Diesel emissions resulted in a similar profile [7]. This pattern is also observed for residential coal burning (anthracite) [7]. The low molecular weight PAH compounds were observed in much lower concentrations for bituminous coal relative to the higher molecular weight PAH [7]. The result of these emissions have lead to the presence of PAH in water supplies. Part-per-trillion quantities have been observed in drinking water [8]. PAH have also been observed in sediments which in turn lead to uptake by shellfish [9]. These compounds have also been observed in smoked foods [10].

This new study examined emission from coal combustion, sewer sludge incineration and a tin refractory operation. The incineration operating conditions are strong factors that influence emission characteristics. The National Incinerator Testing and Evaluation Program (NITEP) was established in Canada to examine operation conditions of municipal incinerator. In a study by the NITEP, two refuse incinerators without control devices were examined at different combustion temperatures [11]. The total PAH emissions decreased by a factor of 1.9 (12490 ng/Nm3 to 6653 ng/Nm3) (ng/Nm3- nanograms per normal cubic meter of air) with a increase in the secondary combustion zone temperature of 300 C (780 C to 1080 C). In addition, total PAH concentrations were shown to decrease across the boiler inlet and stack. This decrease was attributed to transformations.

B. DISCUSSION OF PAH RESULTS

The PAH results presented in the Table IV - XVIII demonstrate a basic pattern of larger concentrations of low molecular weight PAH in the XAD resins. This result was expected and this has occurred in other emission studies [12]. This pattern occurs because lighter PAH compounds with high vapor pressures have the ability to penterate the heated filter section in the gas phase. In addition, these compounds form a weak association with the fly ash. Upon eximination of all sources, essentially all XAD samples contained naphthalene in high concentrations. The identification was confirmed by GC/MS analysis for a Parsippany Troy Hills XAD sample (run #2). Also observed were methyl and dimethyl naphthalenes. The HPLC results for naphthlenes were based exclusively on the less selective UV detector wavelength of 280 nm. Examination of the three sampled runs that comprise each sampled source tends to lack similiarity in terms of PAH identification and concentration.

These variations may be a result of variation in feed stock or operating conditions. If so, the PSE&G source (pulverized coal combustion) should result in the greatest consistency because of the homogeneous feed stock. The first and third runs provide good agreement with respect to identification of similiar PAH compounds but fail in terms of similiar concentrations. Therefore operating temperature fluctuation or sampling variation [13] be responsible. In the PSE&G sample run #2, a significant quantity of benzo(b)fluoranthene (B(b)F) was present while absent in the remaining two runs. In a study by Funcke [14], resins from coal-fired power plants consistently contained large anounts of B(b)F.

The filter sections basically resulted in observation of higher molecular weight PAH compounds. This observation was expected because of the strong association of these compounds with particulate matter. A parallel may be drawn between the appearance of some of the filters and the observed HPLC results. In the cases of the Pequannock Lincoln Park filter samples the appearance of the filter shows an absence of particulate and the HPLC results indicate no PAH compounds in the first two runs and only two low molecular weight PAH in the third run. The Wayne samples contained large quantities of dark soot type particulate and relatively large quantities of fluoranthenes and benzo(ghi)perlyene in runs 2 and 3. In some of the filter samples large quantities of low molecular weight PAH were found to be present. This has most likely occurred because of condensation by restricted movement of material resulting in material build-up on the filters. The washings concentrations of PAH were low but these samples contained a wide range of PAH compounds. The reason for this occurance has resulted from low molecular weight PAH in the impinger solution as a result of condensation and the combination with the train rinse that contained large quantities of particulate matter which are associated with larger molecular weight PAH compounds. Tables IV - XVIII provide total quantities of PAH as a result of sampling. These totals are necessary since the temperature of the filter housing and XAD condenser cartridge can vary, thus changing the distribution of PAH in the sampling unit. It is difficult to characterize any significant differences between the five sampled sources in terms of the NBS 1647 compounds by HPLC analysis. In a study by Bergstrom [12] of emissions by coal, oil and wood such characterization was also unsuccessful. The operating conditions were key to difference observed in the Bergstrom study. Benzofluoranthenes have been observed in the results of the HPLC analysis. These compounds were widely seen in the samples of this study. The concentration values for benzo(b)fluoranthene and benzo(k)fluoranthene specifically were very large relative to B(a)P. B(a)P concentrations were low or undetected. Combustion temperature may be the reason for these relative concentrations. The ratio of Benzofluoranthenes to B(a)P were shown to increase with combustion temperature [7]. Fluidized bed coal combustion is achieved at lower temperatures than pulverized coal combustion. This may explain the non-occurance of B(a)P in the PSE&G pulverized coal source. The plate scanning analysis for benzo(a)pyrene in the XAD resins resulted in comparable concentrations (Table III) for the Parsippany Troy Hills, Pequannock Lincoln Park and Griffin Pipe sources. The results from the Wayne Township source was found to be lower by a factor of six. In comparing the plate scanning results with the HPLC results the Griffin Pipe sample (run #3) did result in quantitation of B(a)P at 8.365 ng/m3 this compared with 5.674 ng/m3 as a result by plate scanning. The fluorescence scanning analysis would not be subjected to possible losses that can occur during transfer procedure in HPLC analysis therefore high values should be found by plate scanning. But the result of the occurrance can be due to interfering materials, such as phthalates, that eluted in the region of B(a)P.

TABLE I
FILTER EXTRACTABLE ORGANIC MATTER
OF
DICHLOROMETHANE AND ACETONE
MILLIGRAMS/FILTER
(MILLIGRAMS/ CUBIC METER)

DICHLOROMETHANE EXTRACTS:

SOURCE	RUN #1	RUN #2	RUN #3	AVG.	STD.DEV
PSE&G STATION	2.200 (0.611)	2.800 (0.912)	2.200 (0.688)	0.737	0.128
PAR-TROY HILLS	8.400 (2.400)	5.400 (1.589)	8.560 (2.518)	2.169	0.413
PEQUANNOCK LINCOLN PARK	2.060 (0.710)	2.320 (0.773)	1.920 (0.640)	0.708	0.054
WAYNE TWP.	24.540 (8.180)	13.600 (4.250)	11.400 (3.563)	5.331	2.034
GRIFFIN PIPE	5.000 (1.645)	5.500 (1.768)	5.600 (1.860)	1.758	0.088

ACETONE EXTRACTS:

SOURCE	RUN #1	RUN #2	RUN #3	AVG.	STD.DEV
PSE&G STATION	3.760 (1.044)	6.620 (2.156)	1.900 (0.594)	1.265	0.656
PAR-TROY HILLS	8.400 (2.400)	8.000 (2.353)	7.800 (2.294)	2.349	0.043
PEQUANNOCK LINCOLN	2.140 (0.738)	2.440 (0.813)	3.540 (1.180)	0.910	0.193
WAYNE TWP.	6.900 (2.300)	9.100 (2.844)	7.800 (2.438)	2.527	0.231
GRIFFIN PIPE	5.440 (1.789)	3.440 (1.106)	2.740 (0.910)	1.268	0.377

TABLE II

XAD EXTRACTABLE ORGANIC MATTER
(DICHLOROMETHANE EXTRACTS)
MILLIGRAMS/GRAM XAD
(MILLIGRAMS/CUBIC METER)

SOURCE	RUN #1	RUN #2	RUN #3	AVG.	STD.DEV.
PSE&G STATION	0.419 (2.128)	0.816 (4.211)	0.448 (2.294)	2.878	0.945
PAR-TROY HILLS	0.624 (3.502)	1.042 (5.452)	0.683 (3.334)	4.096	0.961
PEQUANNOCK LINCOLN PARK	0.100 (0.597)	0.125 (0.753)	0.154 (0.859)	0.736	0.108
WAYNE TWP.	1.035 (5.732)	0.525 (2.873)	0.580 (3.002)	3.869	1.318
GRIFFIN PIPE	0.145 (0.832)	0.349 (1.722)	0.191 (1.107)	1.220	0.372

TABLE III

BENZO(a)PYRENE FLUORESCENCE SCANNING RESULTS FOR XAD EXTRACTS FORM FOUR SOURCES

XAD Samples:	(ng/cubic meter)
Parsippany Troy Hills (run #2)	5.42
Pequannock Lincoln Park (run #2)	6.43
Wayne Twp. Sewerage Authority (run #2)	0.96
Griffin Pipe (run #3)	5.67

TABLE IV

POLYCYCLIC AROMATIC HYDROCARBON HPLC RESULTS BY SAMPLING TRAIN (NG/CUBIC METER)

SAMPLE: Run #1 PSE&G

NBS COMPOUNDS	XAD	FILTER	WASHING	TOTAL
*Naphthalene	292.259		0.985	293.244
**Acenapthylene				
*Acenaphthene				
*Fluorene	36.235			36.235
Anthrancene				
Fluoranthene	48.839		0.196	49.035
**Pyrene			0.275	0.275
Benzo(a)anthracene	71.543			71.543
*Chrysene		9.003	0.063	9.066
Benzo(b) fluoranthene				
Benzo(k)fluoranthene			0.014	0.014
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno (1,2,3-cd)pyrene				

*Note: Selection of these compounds are based on retention time and GC/MS observations or retention time alone. (single HPLC detector wavelength 280 nm)

** -Compound selection based on 280 nm and 365 nm only.

All other compound selection based on 280 nm, 365 nm and fluorescence (excitation 360 nm. : emission > 440 nm).

TABLE V

SAMPLE: PSE&G Generating Station (Run #2)

NBS COUMPOUNDS	XAD	FILTER ******	WASHING	TOTAL
Naphthalene				
Acenapthylene				
Acenaphthene	58.786			
Fluorene				
Anthrancene				
Fluoranthene	8.509			
Pyrene				
Benzo(a)anthracene				
Chrysene			0.107	
Benzo(b)fluoranthene				
Benzo(k)fluoranthene				
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene				

****** - loss of sample during preparation

TABLE VI

SAMPLE: PSE&G Generating Station (Run #3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	43.806	2184.003	0.601	2528.410
Acenapthylene				
Acenaphthene		710.379	5.021	715.400
Fluorene		611.919	1.393	613.312
Anthrancene				
Fluoranthene			0.253	0.253
Pyrene				
Benzo(a)anthracene				
Chrysene			0.181	0.181
Benzo(b)fluoranthene				
Benzo(k)fluoranthene			0.039	0.039
Benzo(a)pyrene			0.066	0.066
Dibenzo(ah)anthracene				
Benzo(ghi)perylene			0.296	0.296
Indeno(1,2,3-cd)pyrene			0.062	0.062

TABLE VII

SAMPLE: Parsippany Troy Hills Serwage Authority Run #1
(ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	7.319	1.408		8.727
Acenapthylene				
Acenaphthene	4629.569			4629.569
Fluorene	81.930			81.930
Anthrancene				
Fluoranthene			0.505	0.505
Pyrene			1.562	1.562
Benzo(a)anthracene				
Chrysene	15.328			15.328
Benzo(b)fluoranthene			0.157	0.157
Benzo(k) fluoranthene	4.504			4.504
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi) perylene	8.408		0.070	18.478
Indeno(1,2,3-cd)pyrene				

TABLE VIII

SAMPLE: Parsippany Troy Hills Sewage Authority Run #2
(ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	9237.515			9237.515
Acenapthylene	1165.369			1165.369
Acenaphthene	9144.360			19144.360
Fluorene	849.783	50.974	0.199	900.956
Anthrancene				
Fluoranthene		6.507	0.331	6.838
Pyrene				
Benzo(a)anthracene				
Chrysene		21.957	0.214	22.171
Benzo(b)fluoranthene			0.153	0.153
Benzo(k)fluoranthene		122.940	0.056	122.996
Benzo(a)pyrene			0.051	0.051
Dibenzo(ah)anthracene				
Benzo(ghi)perylene		118.637	0.083	118.72
Indeno(1,2,3-cd)pyrene			0.068	0.068

TABLE IX

SAMPLE: Parsippany Troy Hills Sewage Authority Run #3 (ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	627.029		0.006	627.035
Acenapthylene				
Acenaphthene	841.229			10841.229
Fluorene	521.678			521.678
Anthrancene				
Fluoranthene				
Pyrene				
Benzo(a)anthracene				
Chrysene			0.075	0.075
Benzo(b) fluoranthene	14.713	4.177		18.890
Benzo(k)fluoranthene				
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene		3.692		3.692

TABLE X

SAMPLE: Pequannock Lincoln Park Sewage Authority Run #1 (ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	830.782		0.434	831.216
Acenapthylene				
Acenaphthene	128.033		0.874	128.907
Fluorene				
Anthrancene				
Fluoranthene	22.989			22.989
Pyrene				
Benzo(a)anthracene				
Chrysene	6.184		0.105	6.289
Benzo(b)fluoranthene			0.005	0.005
Benzo(k)fluoranthene				
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene				

TABLE XI

SAMPLE: Pequannock Lincoln Park Run #2

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
	******			
Naphthalene				
Acenapthylene				
Acenaphthene			1.522	
Fluorene			13.789	
Anthrancene				
Fluoranthene				
Pyrene			0.214	
Benzo(a)anthracene				
Chrysene				
Benzo(b)fluoranthene			0.046	
Benzo(k)fluoranthene				
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene				

****** - note: loss of sample during preparation

TABLE XII

SAMPLE: Pequannock Lincoln Park Run #3 (ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	158.772	74.769	******	
Acenapthylene				
Acenaphthene	74.303	43.962		
Fluorene				
Anthrancene				
Fluoranthene				
Pyrene				
Benzo(a)anthracene				
Chrysene				
Benzo(b)fluoranthene				
Benzo(k)fluoranthene				
Benzo(a)pyrene	3.236			
Dibenzo(ah)anthracene				
Benzo(ghi)perylene	2.216			
Indeno(1,2,3-cd)pyrene				

****** - note: loss of sample during preparation

TABLE XIII

SAMPLE: Wayne Twp. Sewage Authority Run #1 (ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	12893.667		1.528	12895.195
Acenapthylene			0.007	0.007
Acenaphthene			0.749	0.749
Fluorene				
Anthrancene				
Fluoranthene	87.708		0.385	88.093
Pyrene			0.527	0.527
Benzo(a)anthracene				
Chrysene				
Benzo(b)fluoranthene			0.045	0.045
Benzo(k)fluoranthene				
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene				

TABLE XIV

SAMPLE: Wayne Twp. Sewage Authority Run #2 (ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene			0.117	0.117
Acenapthylene				
Acenaphthene	1591.726		0.958	1592.684
Fluorene				
Anthrancene				
Fluoranthene	45.890		0.803	46.693
Pyrene	149.049		0.618	149.667
Benzo(a)anthracene				
Chrysene	138.309		0.058	138.367
Benzo(b)fluoranthene		56.068		56.068
Benzo(k)fluoranthene			0.073	0.073
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene		265.416		265.416
Indeno(1,2,3-cd)pyrene			0.060	0.060

TABLE XV

SAMPLE: Wayne Twp. Sewage Authority Run #3 (ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	111.661	100.779		212.440
Acenapthylene				
Acenaphthene		17.537		17.537
Fluorene		297.199		297.199
Anthrancene				
Fluoranthene	6.195		0.023	6.218
Pyrene				
Benzo(a)anthracene				
Chrysene				
Benzo(b)fluoranthene				
Benzo(k)fluoranthene		19.273		19.273
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene				

TABLE XVI

SAMPLE: Griffin Pipe Scrubber Stack (Run #1)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	8106.375	391.980		8498.355
Acenapthylene			0.341	0.341
Acenaphthene	1182.050		2.496	1184.546
Fluorene		49.361		49.361
Anthrancene				
Fluoranthene	659.567		1.050	660.617
Pyrene	228.764		0.573	229.337
Benzo(a)anthracene			0.129	0.129
Chrysene	80.131	24.621	0.414	105.166
Benzo(b)fluoranthene			0.730	0.730
Benzo(k)fluoranthene				
Benzo(a)pyrene				
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene			0.025	0.025

TABLE XVII

SAMPLE: Griffin Pipe Scrubber Stack (Run #2)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	638.427	718.355	0.110	1356.892
Acenapthylene				
Acenaphthene				
Fluorene				
Anthrancene				
Fluoranthene	623.954	9.030	0.280	45.250
Pyrene	1010.736			1010.736
Benzo(a) anthracene	99.985			99.985
Chrysene	243.275			243.275
Benzo(b) fluoranthene	24.550		0.033	24.583
Benzo(k)fluoranthene				
Benzo(a)pyrene		4.332		4.332
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene		3.197		3.197

TABLE XVIII

SAMPLE: Griffin Pipe Scrubber Stack Run #3 (ng/m3)

NBS COUMPOUNDS	XAD	FILTER	WASHING	TOTAL
Naphthalene	9738.910	54.055	0.741	9793.706
Acenapthylene	5567.787			5567.787
Acenaphthene	42690.936	107.710		42798.646
Fluorene			0.301	0.301
Anthrancene				
Fluoranthene	1044.194		0.287	1044.481
Pyrene			0.126	0.126
Benzo(a) anthracene	34.058			34.058
Chrysene			0.127	0.127
Benzo(b) fluoranthene	11.176			11.176
Benzo(k)fluoranthene			0.013	0.013
Benzo(a)pyrene	8.365		0.036	8.401
Dibenzo(ah)anthracene				
Benzo(ghi)perylene				
Indeno(1,2,3-cd)pyrene				

IV. NITRO-PAH COMPOUNDS

A. NITRO-PAH INTRODUCTION

Nitro-PAH compounds have been shown to contribute a significant part of the direct acting mutagenic properties found in airborne particulate matter. These compounds are highly mutagenic in the Ames Assay. Compounds such as 1-nitropyrene have been observed in diesel emissions [15], residential wood burning [16] and coal combustion [17]. Many nitro-PAH compounds have only been observed in air samples as the result of nitrating species in the atmosphere. The approach taken in many studies has been to examine the reactivity of PAH with nitrating species in addition to mechanisistic investigation. The nitration of pyrene to 1-nitropyrene was examined by Pitts [18]. The study defined dinitrogen pentoxide as a very strong nitrating agent. Nitrogen Dioxide and nitric acid was found to nitrate pyrene to a much lesser extent. The nitration of perylene to 3-nitroperylene occurred to a smaller extent in the presence of even the strongest agent (dinitrogen pentoxide). These observations were the result of exposing pyrene and perylene on glass fiber to the nitrating agents. In order to examine nitration reactions under conditions closer to that of atmospheric, Ramdahl [19] exposed different surface carriers (silica, alumina and charcoal) to nitrogen dioxide. Different surfaces have stabilized PAH from nitration to various extents. The lowest reactivity occurred on the charcoal surface and the highest on the silica surface.

B. NITRO-PAH RESULTS

The nitro-PAH analysis of the incinerator samples was based on the National Bureau of Standards reference material (NBS 1587). The NBS 1587 compounds were not observed in any of the emission samples. These compounds are found in very low concentrations compared to the PAH compounds. The initial negative results in individual samples were followed by extensive compositing of samples from a given source. This involved compositing numerous runs of XAD resin extracts, filter extracts and washings. The selected GC/MS analysis also failed to identify nitro-PAH compounds.

In a study conducted by Olsen [20] flue gases were examined by adsorption to tenax. The emissions were a result of coal combustion. Three grades of coal were combusted in different size plants. In all cases 1-nitropyrene was observed in emissions from the plants. Concentrations varied for the plants from 29 ng/m3 to 608 ng/m3. When comparing these results with the results from the PSE&G coal source of this study it is apparent that Olsen also quantitified large amounts of pyrene (392 to 1340 ng/m3) and no pyrene was observed in the PSE&G samples by HPLC or GC/MS. Therefore the lack of the precursor must be the reason for no detection of 1-nitropyrene. Pyrene was found in the sewer sludge incinerator emissions of Wayne Twp. and the refractory emissions at Griffin Pipe but no 1-nitropyrene was observed. The condition are most likely unfavorable for nitration to occurs in terms of the amount of time required or in term of the nitrating species present.

C. QUINONE-PAH

The quinone-PAH analysis by HPLC has failed to show the presence of perinaphthenone, anthraquinone, 4,5-benzo(a)pyrenedione, or 1,6-benzo(a)pyrenedione. The preliminary analysis of separate samples was subsequentally followed by extensive compositing as was performed in the nitro-PAH analysis. This procedure as well as GC/MS analysis has failed to result in positive identification of these compounds. These compounds were observed in airborne particulate matter [1].

V. DIOXIN/FURAN SECTION

ABBREVIATIONS OF TERMS

TCDD	tetrachloro-p-dibenzodioxin	(family)
PCDD	pentachloro-p-dibenzodioxin	" "
H6CDD	hexachloro-p-dibenzodioxin	" "
H7CDD	heptachloro-p-dibenzodioxin	" "
OCDD	octachloro-p-dibenzodioxin	

TCDF	tetrachlorodibenzofuran	(family)
PCDF	pentachlorodibenzofuran	" "
H6CDF	hexachlorodibenzofuran	" "
H7CDF	heptachlorodibenzofuran	" "
OCDF	octachlorodibenzofuran	

A. DIOXIN/FURAN INTRODUCTION

The formation of polychlorinated dibenzo-p-dioxins and dibenzofurans (hereafter termed "dioxins and furans") are a major concern due to their extreme carcinogenic potency. These potency values are a result of animal studies. The slope of the dose response curve is equal to the potency. The slope is determined from the plot of number of the animals that develop tumors versus administered concentration of dioxin. The slope (carcinogenic potency) is found to be extreme for dioxins in comparision to other carcinogens administered in similar animal studies. Carcinogens that are shown to be causally associated with induction of cancerous tumors in humans are designated as known human carcinogens. When these compounds (such as vinyl chloride, benzene, bis-chloromethylether) are administreed to animals, the resulting slope of the dose response curve is much smaller that those obtained from dioxin exposure in similar animal studies. Dioxins and Furans are not mutagenic substances. Their mode of action is believed to occur by an interaction with cytolic (soluble enzyme fraction) receptor protein which has a high affinity for tetra-p-dibenzodioxin (TCDD). The 2,3,7,8 TCDD isomer which is symmetrical and planar is believed to result in the strongest interaction of all TCDD isomers [21]. The sources of dioxins and furans include by-products of 2,4-dichlorophenoxyacetic acid (2,4-D) and

2,4,5-trichlorophenoxyacetic acid (2,4,5-T) production, formation as a result of transformer explosions which contain polychlorinated biphenyls, incineration of materials that contain dioxin precursors or unrelated chlorinated materials. Dioxins were first seen in particulates from incinerators in 1977. Today, concerns are raised over the problem of mounting wastes and landfill limitations. Although incineration seems to be a viable solution, dioxin emissions are currently regarded as the key issue hindering this method of disposal. In order to minimizes these problems new incinerators are constructed which utilize new emission controls. These controls include scrubbers with lime sprays that reduce HCl (hydrochloric acid) and cool gases allowing adsorption to particulates. The particulates are then trapped by bag house filters which have the advantage of removing particulates more efficiently as operation continues. This occurs because a cake builds up and filters smaller particulates. Electrostatic precipitators (ESP) are at a disadvantage because increased operation decreases efficiency by particulate build up. In addition small particles are more difficult to trap. It is these particles that are detrimental to health because of deep lung penetration. Formation of dioxins and furans can occur in even very efficient incinerators that operate at high temperatures considered favorable for dioxin destruction. The formation results from cooler zones (secondary formation) that exist in these incinerators. The feed stock also plays a major role in dioxin/furan formation. Non-combustible materials such as polyvinylchloride (PVC) contain plasticizers and HCl that can promote dioxin chlorination. In a study conducted by the U.S. Environmental Protection Agency (EPA), the presence of PVC and polyethylene in a rotary kiln at 1950 F and 100% excess air has resulted in the formation of dioxin and furan precursors (1,2,4-trichlorobenzene and pentachlorophenol). In addition, significant quantities of dioxins and furans were observed. Incineration feed stocks that exclude non-combustable materials such as PVC show significant reductions in dioxins and HCl emissions. The New York Department of Environmental Conservation has determined that U.S. refuse incinerators produce more than forty times the HCl found in coal burning facilities. This is attributed to incombustible chlorinated materials including PVC. Some Japanese incinerators show almost non-detectable quantities of HCl because of the sorting out of non-combustable materials [22]. The sorting process can also reduce other toxic emissions that are of environmental concern.

The mechanism for dioxin and furan formation has not been completely elucidated. The most widely accepted mechanism is based upon surface reactions. These reactions occur on the surface of particulate matter known to contain inorganic substances that are thought to catalyze the reactions. Different surfaces should vary in their effectiveness in catalyzing dioxin formation the result of variations in amounts and types of inorganic species present, various particulates could be tested to validate the surface mechanism. This is the nature of a study conducted by Karasek and Dickson [23]. Fly ash was taken from the ESP of municipal incinerators and later stripped of organic material. The fly ash samples were then placed in a heated reservoir containing labeled pentachlorophenol to bring about the formation of dioxin and furans. Fly ash samples were obtained from a municipal refuse incinerator in Toronto, Canada, a modern fluidized bed municipal refuse incinerator in Machida, Japan and an effluent stream of a copper refinery in Noranda, Canada (Ground copper wire with PVC insulation was present in the combustion operation). Fifty gram amounts of fly ash from each of the sources was placed in a reservoir. Carbon 13 labeled pentachlorophenol is passed through the reservoir at 300 C. A nitrogen stream is passed through the reservoir at 10 ml/minute. The results are shown in Table XIX.

TABLE XIX
DIOXIN FORMATION FROM A LABORATORY REACTOR CONTAINING VARIOUS SUPPORT SURFACES

(Karasek and Dickson)

Source	TCDD	P5CDD	H6CDD	H7CDD	OCDD
Ontario fly ash*	218±117	571±225	1041±119	1559±486	430±221
Machida fly ash*	54	115	121	132	40
Noranda fly ash				11	18
Groundfire brick**					4
Empty*** reservoir					267

* - chlorine and metallic elements present

** - provides surface only

*** - no surface support present

The results demonstrate the variation of dioxin formation with variation in surface. In a closer examination of the fly ash surfaces by x-ray photoelectron spectroscopy (XPS) the Ontario and Machida fly ash are shown to contain chlorine and metallic elements that are absent on the Noranda fly ash. In order to see if large surface area alone could be responsible for dioxin formation fire brick was placed in the reservoir apparatus. The results show a trace level formation of the octachlorodibenzodioxin (4 ng). Therefore surface alone did not lead to significant dioxin formation. Also the reservoir without any support material was operated . The results show a sufficient amount of the octachlorodibenzodioxin. This is thought to occur due to the condensation of two pentachlorophenol molecules. The factor of temperature was also examined using the Ontario fly ash since it had the highest catalytic activity (Table XX).

TABLE XX
TEMPERATURE EFFECT OF DIOXIN FORMATION FROM LABORATORY REACTOR
CONTAINING ONTARIO FLY ASH
(100 micrograms of carbon-13-labeled pentachlorophenol was added in each case)
(Karasek and Dickson)

	Amount of Dioxin Congeners (ng.)				
Temp. (C)	TCDD	P5CDD	H6CDD	H7CDD	OCDD
250			29	583	3463
300	218	571	1041	1559	430
340	61	228	392	384	50
400	8	17	34	70	14

The maximum yield occurred at 250 C but at 300 C significant amounts of the lower chlorinated dioxins were observed. At 400 C destruction began to result, reducing the formation of all dioxins (tetra through octa). The Ontario fly ash was also reacted with 400 ng of carbon-13-labeled phenol. Chlorination would require removal of chlorine from inorganic compounds on the fly ash. This resulted in the formation of 234 ng tetrachloro-dioxin, 63 ng of the pentachlorodioxin and 7 ng of hexachlorodioxin. This study provides insight into dioxin formation although conditions that exist in an actual incinerator may include other formation or destruction pathways and the precursors in actual incinerators are of various types. The pentachlorophenol compound is of interest because of its use as a wood preservative; it has also been observed in sewer sludge samples. It may be the source of dioxin emission through insufficient destruction.

There have been numerous correlations made between observed conditions in individual studies and the extent of dioxin/furan formation [25]. In one such study by Roger D. Griffin [24] attempted to explain dioxin/furan formation through use of thermodynamic quantities for the exploration of possible mechanisms. The approach was to study why coal combustion resulted in lower emissions than municipal solid waste (MSW) combustion. The compositions of the feed stocks were evaluated. The ratio of chlorine to sulfur for coal is approximately 0.2 and that of MSW is between 2.5 and 3.5. Using basic thermodynamic analysis of reactions it was determined that the chlorination of benzene (used as a typical aromatic precursor) is unfavorable ($\Delta G = +34$ Kcal).

$$C_6H_{6\,(g)} + 2\,HCl_{(g)} \longrightarrow C_6H_4Cl_{2\,(g)} + H_{2\,(g)}$$

If oxygen is placed in the reaction equation, the reaction becomes favorable thermodynamically.

$$C_6H_{6(g)} + 2\,HCl_{(g)} + \frac{1}{2}\,O_{2(g)} \longrightarrow C_6H_4Cl_{2(g)} + H_2O_{(g)}$$

TABLE XXI

DOW CHEMICAL COAL EXPERIMENTS (IN AIR AT 600 C)

REACTANTS RATIO	TOTAL Cl, mg	DIOXIN LEVELS, ng/g	Cl/S
Coal	1.6	1.9	0.1
Coal+HCL	79.0	99.0	4.0
Coal+CL2	132.0	411.0	6.6

Combustion efficiency has also been shown to be a major factor in dioxin/furan emissions although some studies have reported exceptions to this view. In a study by Hasselirils [25] total dioxin/furan emissions were higher either under conditions of excessive oxygen or insufficient oxygen. This correlated with decreases in combustion efficiency (CE) as conditions were displaced from those of the optimized state. The study was carried out in an incinerator that excluded incombustible materials. The lowest dioxin/furan emissions were observed at the highest combustion efficiency. A study by Bergstrom [26] also confirmed that CE plays a major role in the production of micro-pollutants such as polycyclic aromatic hydrocarbons (PAH), chlorobenzene, chlorophenols and dioxin/furans. This study utilized an isokinetic sampling unit (a unit that collects material that is representative of the emitted form with sampling rates that do not alter flow of material) with a filter, XAD-2 sorbent and condensate fractions.

The moisture content of the incinerator feed stock is still another factor influencing dioxin/furan emission. Moisture increases result in reduction of furnace temperatures. This in turn leads to favorable conditions for dioxin/furan formation. This can occur by insufficient destruction of dioxin/furans and also can result in the formation of cooler zones for secondary dioxin production by dioxin precursors. This is a significant problem in resource recovery facilities because of the fluctuation of the feed stock. Maintaining an adequate temperature requires variation in the rate of air influx corresponding to variations in moisture of the feed stock. The operation of these energy recovery facilities also requires avoiding temperature that are too high. This is necessary for proper operation because temperature exceeding 2000 F can result in boiler tube fouling and in turn reduced heat transfer. In addition, emissions of NOx compounds may significantly increase. These boundary conditions reduce the range of operating conditions for sufficient dioxin/furan destruction. Other factors that influence the operation of such incinerators are time and gas turbulence. Particulate matter may become entrained and in turn the gases can strip the compounds and increase gaseous emissions. The turbulence of the gases can result in imbalances in movement of material to cooler zones and areas of depleted oxygen. An interesting observation is the reduction in dioxin/furan formation by the addition of ammonia to incinerator operations. Ammonia was employed to reduce NOx emissions in a resource recovery facility in Commerce, California and subsequently, extremely low dioxin emissions were observed. Ammonia is believed to interfere with dioxin/furan formation by poisoning the catalytic ability of the particulate components. This is consistent with observations of high dioxin emission from a copper reclamation facility (where PVC coated copper is burned). Metal halides such as copper chlorides Cu(I) and Cu(II) [27] are believed to be responsible for the catalytic activity. A conflicting result [22] was reported wherein no changes were observed in emission with addition of ammonia but significant reductions with the introduction of carbon disulfide. The investigators also attribute this result to poisoning of the metal halide catalyst. However, a question immediately arises concerning this result and its consistency with the Griffin study [28]. It may just be sulfur playing a role in reducing the chlorination steps by unfavorable thermodyamics of direct chlorination instead of catalyst poisoning. In addition the dioxin/furan concentration in fly ash from municipal incinerators are found to be higher than that in the bottom ash. The fly ash is more of a concern because of its release due to the limited effectiveness of controls. There are many contradicting reports about total dioxin/furan emission. This is a result of studies that utilize fly ash as the total emission factor. The more comprehensive approach is to collect flue gas condensate in addition to fly ash since significant volatilization can occur from particulate matter. The flue gas can be a major contributor to the total dioxin/furan emissions [29] . Fly ash samples subjected to dioxin/furan analysis are almost invariable obtained from some particulate control such as a electrostatic precipitator. Work by Tong and Karasek [30] examined fly ash samples from seven municipal refuse incinerators in four different countries. The dioxin/furan isomer pattern was very similar in all samples. This occurred even though feed stocks varied.

TABLE XXI

DIOXIN/FURAN CONTENT IN FLY ASH SAMPLES FROM INCINERATORS

(Tong and Karasek)

LOCATION	TCDD	P5CDD	H6CDD	TCDF	P5CDF	H6CDF
Ontario	436	504	668	294	508	420
Oslo	27	77	149	55	74	80
Paris	18	50	142	81	136	192
Kyoto	8	17	38	15	23	22
Hiroshima	29	95	149	90	92	85
Manchida	0.2	0.8	4	2	7	12

The thermal behaviors of fly ash samples were examined by Vogg and Stieglitz [31]. Again fly ash samples were obtained from an electrostatic precipitator. The samples were placed in crucibles and heated in a furnace to 120, 200, 300, 400, 500 and 600 C for two hours. The samples were then analyzed for dioxins and furans. Sudden increases in all congeners were observed at 300 C followed by large decreases at higher temperatures. This is due to destruction. Even though the two hour heating heating is a laboratory procedure in this study actual particulate may remain inside a incineration system by lining boiler tubes or other components of the system. Therefore, their experimental design does somewhat simulate actual incineration conditions.

Fly ash samples taken from ten municipal waste incinerators in Germany were examined for dioxins and furans in a study by Hagenmaier [32]. The study consisted of fifty-two fly ash samples.

TABLE XXIII

SUMMARY OF DIOXIN/FURAN ANALYSES FROM TEN WASTE INCINERATORS

(ng/g fly ash)

(Hagenmaier)

	MINIMUM	AVERAGE	MAXIMUM
TCDD	0.1	11	67
P5CDD	0.3	34	201
H6CDD	0.4	50	253
H7CDD	0.3	57	260
OCDD	0.2	65	365
TOTAL	1.3	210	861
TCDF	0.7	72	477
P5CDF	0.8	95	494
H6CDF	0.3	82	404
H7CDF	0.1	56	386
OCDF	0.02	13	174
TOTAL	1.9	275	1660

Also in this study dioxin/furan concentrations are shown to vary by more than a factor of ten when examining two different municipal waste incinerators. In many studies the amount of furans detected are shown to be considerably higher than that of the dioxins. This pattern is thought to result from structural differences. The destruction at high temperatures is thought to occur by cleaving the carbon-oxygen bonds. The dioxins have two such points of attack while the furans provide only one site.

II. RESULTS AND DISCUSSION

The dioxin and furan samples for this project were obtained from five incineration sources.

1.) PSE&G GENERATING STATION (MERCER) BOILER #1
(pulverized coal operation)

2.) PARSIPPANY TROY HILLS SEWERAGE AUTHORITY
(sewer sludge feed stock)

3.) PEQUANNOCK, LINCOLN PARK AND FAIRFIELD SEWAGE AUTHORITY [INCINERATOR (N.J. STACK no. 001)]
(sewer sludge feed stock)

4.) WAYNE TWP. SEWAGE AUTHORITY
MULTIHEARTH INCINERATOR
(sewer sludge feed stock)

5.) GRIFFIN PIPE CUPOLA SCRUBBER STACK
(gray tin foundary)

The sampling was conducted by the New Jersey Department of Environmental Protection (NJDEP). The procedure utilized the U.S. EPA Modified Method 5 sampling procedure. The sampling train consisted of XAD amberlite resin, filters and washings (impinger and train rinse). The resin samples were removed from their traps and weighed. Twenty-five percent of the resins were reserved for dioxin testing and the remanding portion was used for PAH, nitro-PAH and quinone-PAH analysis which was conducted at the New Jersey Institute of Technology (N.J.I.T.). The filter samples were cut in half reserving half for dioxin/furan analysis. The washings consisted of front and back sections for each run. The front and back sections were first combined and then separated into equal volumes. Half was reserved for dioxin/furan testing. The dioxin/furan testing was conducted by The Environmental Testing and Certification Corp. (ETC) of Edison, New Jersey. The resin samples were analyzed in accordance with the EPA SW-846 method 8280. The samples consisted of three runs for each source. The analysis was conducted by compositing three runs from each source. For resins three 25% portions comprised one sample. For filters three half filters comprised the filter samples. For washing three half volumes comprised one sample analyzed. The dioxin/furan analysis was performed for detection of the tetra through octa families. In addition analysis was conducted to quantify the specific 2,3,7,8 dioxin and 2,3,7,8 furan isomers.

TABLE XXIV

RESULTS OF DIOXIN/FURAN ANALYSIS

The following positive results were observed:

Parsippany Troy Hills:	XAD (ng/m3)	FILTER	WASHINGS
TCDD (family)	3.043	ND	12.88 (pg/m3)
TCDF (family)	ND	ND	22.02 (pg/m3)
PS&G Generating Station:			
H7CDD (family)	ND	0.316	ND

Note: The following Tables XXIV - XXIX present the negative dioxin/furan results.
ND-no detection
Units are given in ng/m3 unless otherwise indicated

THE FOLLOWING TABLES PRESENT THE NEGATIVE
DIOXIN/FURAN RESULTS
DIOXIN/FURAN DETECTION LIMIT DATA

SAMPLE: Pequannock Lincoln Park XAD Resin (Runs 1-2-3)

	(ppb)
2,3,7,8-TCDD	0.06
TCDD	0.06
PCDD	0.18
H6CDD	0.26
H7CDD	0.31
OCDD	0.16
TCDF	0.06
PCDF	0.26
H6CDF	0.35
H7CDF	0.27
OCDF	0.13

TABLE XXVI

SAMPLE: Wayne Twp. Sewage Authority (Runs 1-2-3) XAD Resins

	(ppm)
2,3,7,8-TCDD	0.26
TCDD	0.26
PCDD	0.82
H6CDD	1.4
H7CDD	0.86
OCDD	0.25
TCDF	0.19
PCDF	0.53
H6CDF	1.2
H7CDF	1.0
OCDF	0.24

TABLE XXVII

SAMPLE: Griffin Pipe (Runs 1-2-3) XAD Resins

	(ppm)
2,3,7,8-TCDD	0.16
TCDD	0.16
PCDD	0.57
H6CDD	0.87
H7CDD	0.82
OCDD	0.21
TCDF	0.16
PCDF	0.52
H6CDF	1.2
H7CDF	0.83
OCDF	0.25

TABLE XXVIII

SAMPLE:	Blank XAD (ppm)
2,3,7,8-TCDD	0.47
TCDD	0.47
PCDD	1.4
H6CDD	1.9
H7CDD	2.4
OCDD	0.35
TCDF	0.38
PCDF	9.5
H6CDF	2.2
H7CDF	1.8
OCDF	0.38

TABLE XXIX

SAMPLE: Parsippany Troy Hill Sewage Authority (Runs 1-2-3) Washing Samples

	(ppt)
2,3,7,8-TCDD	20.1
TCDD	-
PCDD	27.6
H6CDD	25.4
H7CDD	42.3
OCDD	22.4
TCDF	-
PCDF	31.1
H6CDF	7.63
H7CDF	14.5
OCDF	60.5

Table XXIV presents positive results for the Parsippany Troy Hills XAD resin and washing. The XAD resin concentration of 3.043 ng/m3 accounts for all tetrachloro-p-dibenzodioxin (TCDD) isomers. Inaddition specific analysis for the 2,3,7,8 TCDD isomer resulted in no detection. The results point towards exclusive association of TCDD with the gas phase since the washing also contained TCDD but not the filter. Although gas stripping of TCDD from fly ash may occur during sampling it is unlikely to be so efficient as to strip all material.

For the PSE&G source only the PSE&G filter sample tested positive for the heptachloro-p-dibenzodioxin family. This may occur due to a strong association of fly ash with higher chlorinated dioxins.

APPENDIX: SAMPLING TRAIN UNIT AND STANDARD CHROMATOGRAMS

FIGURE 1.

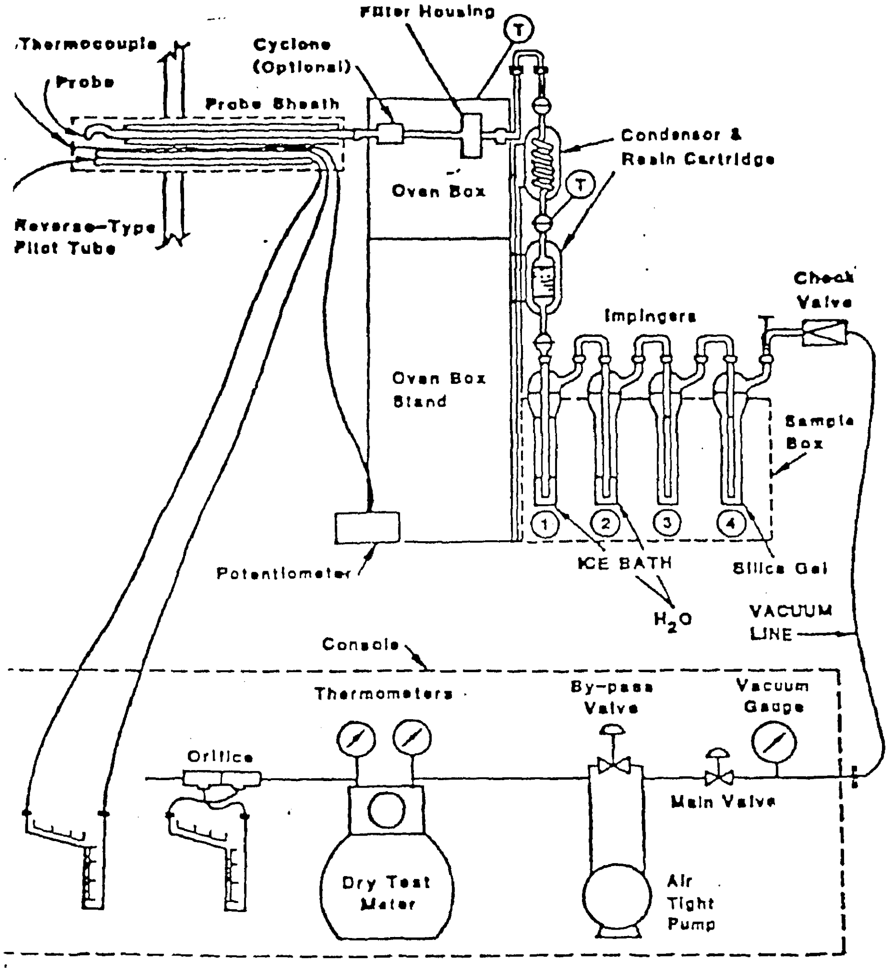
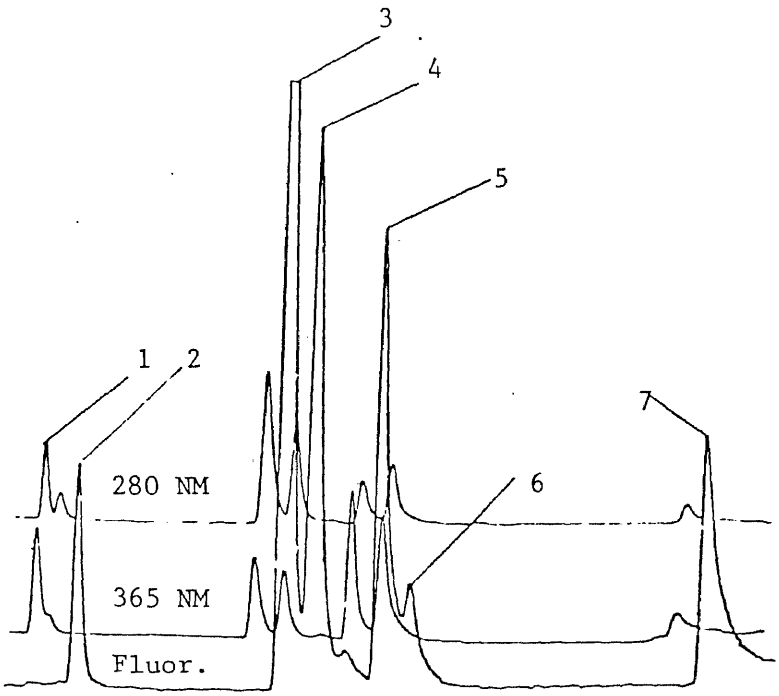

Filter Housing
Thermocouple
Cyclone (Optional)
Probe
Probe Sheath
Condensor & Resin Cartridge
Oven Box
Reverse-Type Pitot Tube
Check Valve
Impingers
Oven Box Stand
Sample Box
Potentiometer
ICE BATH
Silica Gel
H_2O
VACUUM LINE
Console
Thermometers
By-pass Valve
Vacuum Gauge
Orifice
Main Valve
Dry Test Meter
Air Tight Pump
T
1
2
3
4

FIGURE 2.

HPLC OF NBS SRM 1587 NITRO-PAH
WITH REDUCER COLUMN

1 : 2-Nitrofluorene
2 : 9-Nitroanthracene
3 : 3-Nitrofluorene
4 : 1-Nitropyrene
5 : 7-Nitro B(a)A
6 : 6-Nitrochrysene
7 : 6-Nitro B(a)P



FLUOR: 395 EXCIT; 460 EMISS

FIGURE 3

HPLC OF QUINONES WITH REDUCER COLUMN

1 : 4,5 Bep/D
2 : 4,5 Bap/D
11,12 Bap/D
3 : 7,8 Bap/D
4 : 6,12 Bap/D
1,6 Bap/D
5 :3,6 Bap/D
6 :7,10 Bap/D

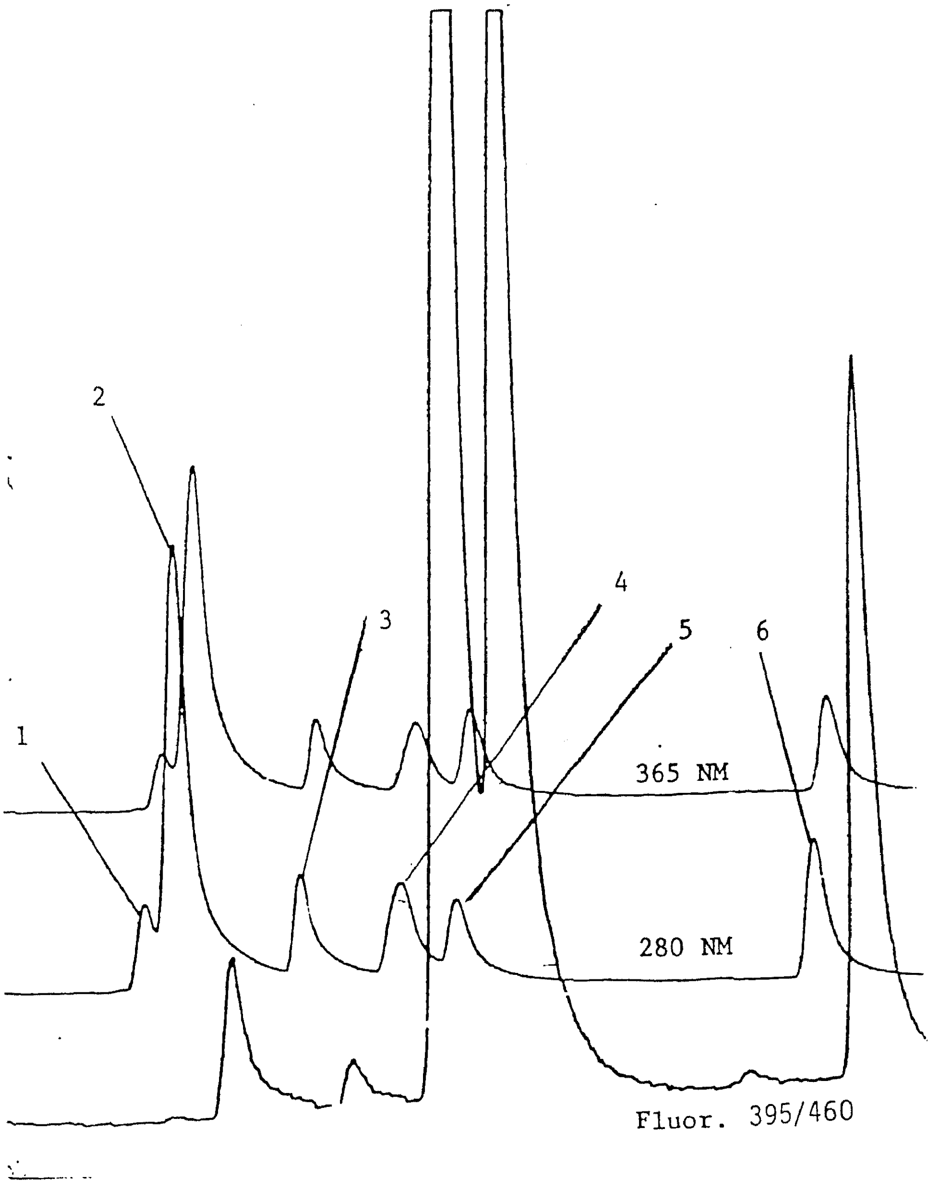
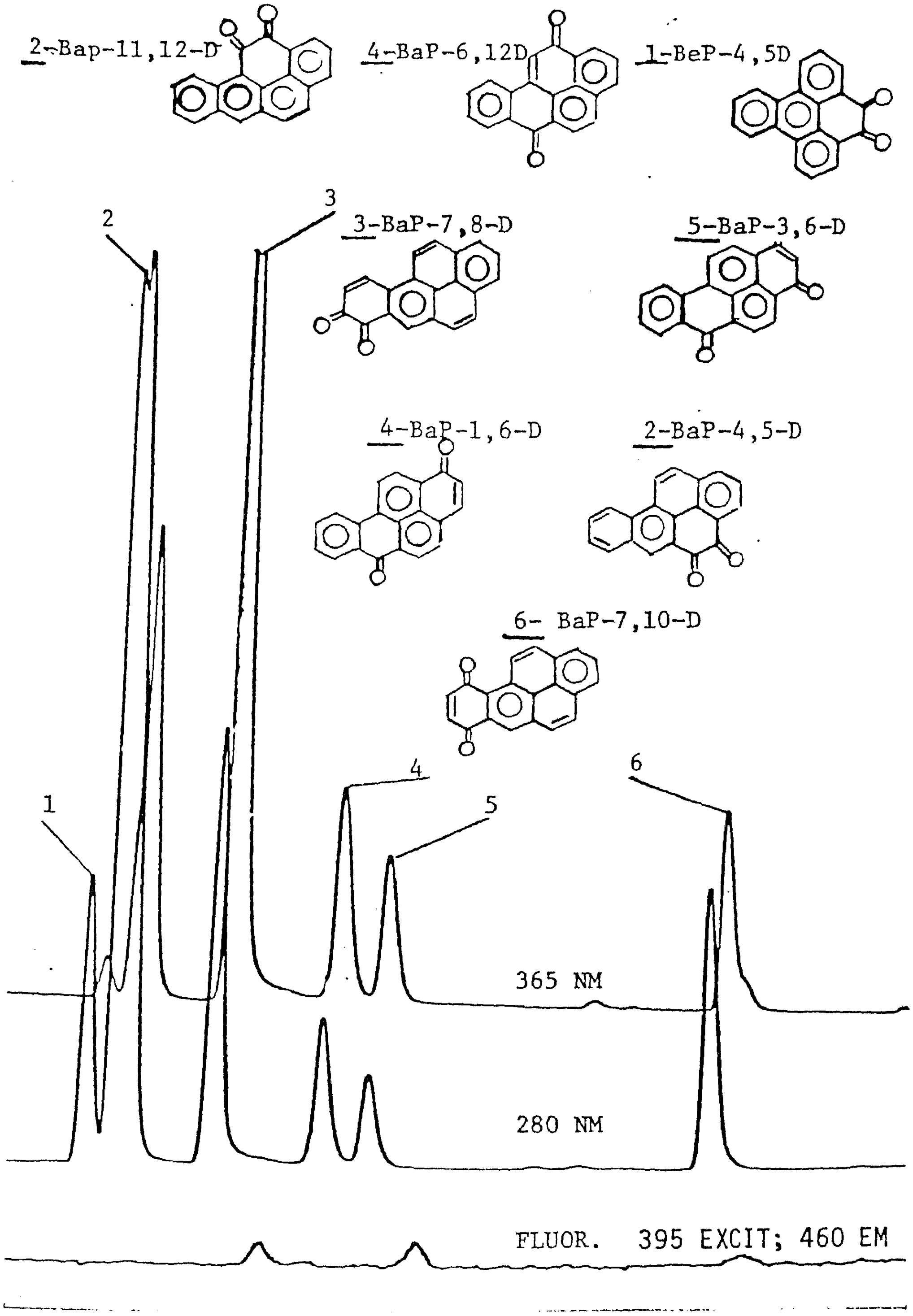


FIGURE 4 HPLC OF QUINONES WITHOUT REDUCER COLUMN



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