

Applicability of a Cryogradient Technique for the Enrichment of PAH from Automobile Exhausts: Demonstration of Methodology and Evaluation Experiments

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A cryogradient system for the enrichment of polycyclic aromatic hydrocarbons from gasoline and diesel powered vehicles is described. The sampling involves particle trapping on a filter followed by gas phase enrichment in three separate condensers.

The filter is extracted with dichloromethane (DCM). For the extraction of the condensers three different solvents have been used; cyclohexane, acetone and DCM. The latter has also been used together with three buffers, pH 3, pH 7 and pH 11. Analyses of polynuclear aromatic hydrocarbons were performed by means of glass capillary gas chromatography and mass spectrometry. These analyses of diluted gasoline exhausts show that of the phenanthrene/anthracene, fluoranthene/pyrene and their monoalkylated forms found, between 90 and 30% are present in the gas phase. For diesel emissions, corresponding values are between 50% and 5%, respectively. However, the distribution of PAH between gas phase and particles is dependent on dilution ratio and filter temperatures.

The addition of NO₂ (approximately 7 ppm) prior to filter sampling involves degradation of cyclopenteno(cd)pyrene (CPcdP) and benzo(a)pyrene (BaP) on the particles from diluted gasoline exhausts. This also occurs with BaP on diesel particles sampled under equivalent conditions. Mutagenicity data from these experiments support the theory of formation of direct-acting mutagens, probably due to nitration. Parallel sampling of particles with Teflon-coated and glass fiber filters does not show that components which are reactive to NO₂, e.g., CPcdP, are degraded to a lower extent when glass fiber filters are used.

Introduction

Incomplete combustion of fossil fuels is a significant source of polycyclic aromatic hydrocarbons, PAH, and in the mid 50s the first attention was paid to the possibility that the growing population of motor vehicles, both with diesel and gasoline engines, could contribute to the PAH found in ambient air.

Total Raw Gas Sampling

A comprehensive review of different sampling methods for PAH from automobiles is presented

elsewhere in this issue (1). Only some principles will be described here.

A general approach was given by Stenberg et al. (2) when they used condensation before filtering, and this technique was later adapted by several investigators and has proven to be very useful. In 1962 Begeman and Colucci (3) described a sampling system with a steel condenser which enabled the collection of both gaseous and particle-associated PAH. Grimmer et al. in 1972 introduced (4) a modified construction with the use of a vertical glass condenser, and an improved type with an increased cooling capacity has recently been presented by VW (5).

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Proportional Raw Gas Sampling

The collection of the total exhaust volume will make the subsequent work time consuming, but one way to circumvent the large sample amount is by using proportional sampling (6-8). This technique allows the handling of a small sample, and has become an interesting alternative with the development of more sensitive analytical methods and biological tests *in vitro*.

Dilution Tunnel

The previously described sampling methods utilized raw gases for the determination of PAH. However, a technique has been developed in order to simulate reactions of gases and particles when mixed with ambient air: a so-called dilution tunnel (9). With the employment of this dilution technique, it is anticipated that gas-phase components—and among these certain PAHs—will adsorb on particles, or that certain chemical reactions take place before sampling. Thus, this would give a sample of more "true" composition than otherwise. The residence time within a tunnel differs but is probably less than 5 sec in most cases. Recently it has been shown that PAHs, even after dilution, are present in the gas phase in the emission from a gasoline vehicle (10-12). The enrichment methods employed have been either adsorbent trapping (11) or a cryo technique (10,12,13).

The results reported in this paper are based on samples obtained with a cryogradient sampling system for the enrichment of gaseous PAH and derivatives of these, in combination with conventional particle trapping on glass fibre filters. Samples have been taken from both gasoline and diesel exhausts, which have been diluted in a tunnel.

Materials and Methods

Sampling System

The sampling equipment shown in Figure 1, consists of a thermostatted filter holder; an ice/water condenser, cooling area 0.55 m²; a CO₂/ethanol condenser, cooling area 0.60 m²; a liquid nitrogen condenser, cooling area 0.75 m²; a pump system with flow elements, temperature/pressure sensors, valves and dry gas meter (see Fig. 2).

The filter holder and cooling equipment are mounted on a mobile rack of approximately 2 m height and the pumping system on a trolley. All parts in contact with the sample stream are made of stainless steel, Teflon or glass. The ice/water condenser (Fig. 3) is equipped with two jackets and two

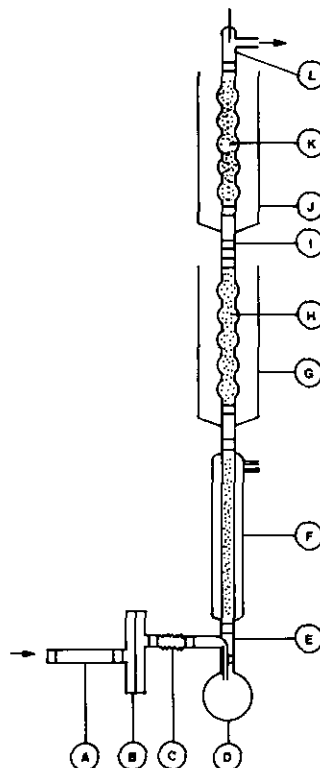


FIGURE 1. Sampling equipment: (A) flexible metal tubing, 250 mm, (B) filter holder, diameter 127 mm, stainless steel; (C) Teflon bellows; (D) round-bottomed flask, 1000 mL; (E) normal glass joint; (F) ice/water condenser; (G) cryo vessel, dry ice/ethanol; (H) condenser cartridge; (I) ball glass joint; (J) cryo vessel, liquid nitrogen; (K) condenser cartridge; (L) Teflon/glass joint, temperature sensor.

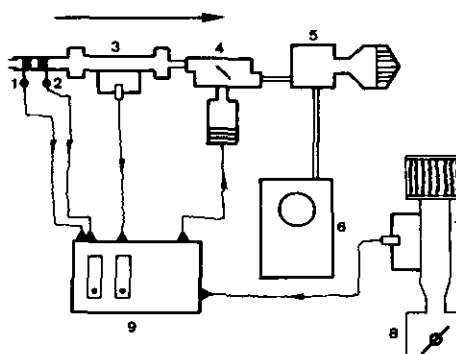


FIGURE 2. Pump and feed-back system: (1) temperature sensor; (2) pressure sensor; (3) laminar flow element; (4) valve; (5) pump; (6) dry gas meter; (7) laminar flow element (air filter); (8) carburetor; (9) electronics.

coils and filled with glass beads. The cooling reservoir (20 liter) is connected to two Eheim pumps giving 3 L/min. The dry ice/ethanol condenser (Fig. 4) is made of glass and filled with glass beads and

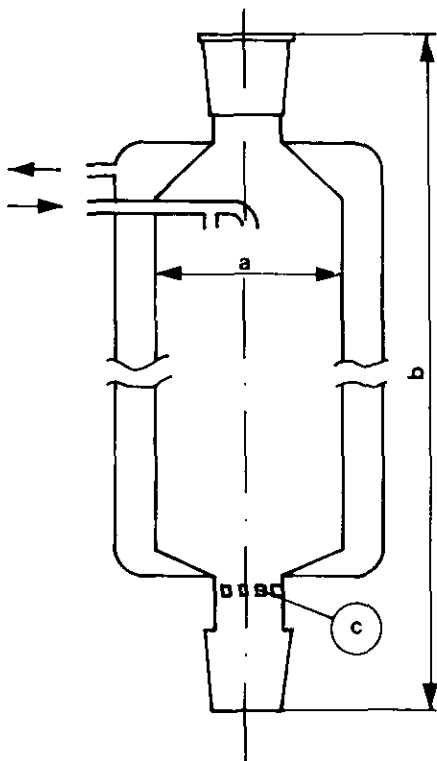


FIGURE 3. Ice/water condenser. Pyrex glass, filled with glass beads of 6 mm. diameter; (a) 70 mm; (b) 440 mm; (c) fritted glass disc.

rings. The liquid nitrogen condenser is of the same type but with glass beads of smaller size.

The cryogenic vessels (Fig. 5) are made of glass and insulated with polyurethane foam in two layers. The cooling down period is approximately 45 min and the temperature is kept constant by adding more dry ice and liquid nitrogen, respectively. The pumping unit can be used either as a proportional sampler, using a reference signal from the carburettor, or as a constant flow sampler compensating for the pressure drop. Maximum sampling velocity is 100 L gas/min.

Laboratory Tests

Before sampling authentic automobile exhausts, the utility of the system was evaluated by different laboratory tests. For this purpose a small dilution tunnel was built in order to generate different artificial sample streams. This laboratory dilution tunnel comprises a gas washing flask with a glass tube on the outlet (350 × 30 mm diameter). The washing flask was filled with different liquid compounds which were volatilized by purging purified nitrogen through the liquid. The flask was immersed

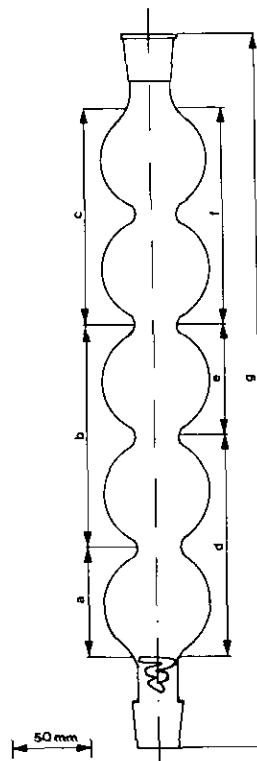


FIGURE 4. Condenser cartridge. Pyrex glass; dry ice/ethanol: (a) 8 × 8 mm rings; (b) 6 × 6 mm rings; (c) 5 mm diameter beads. Liquid nitrogen: (d) 6 × 6 mm rings; (e) 5 mm diameter beads; (f) 2 mm diameter beads.

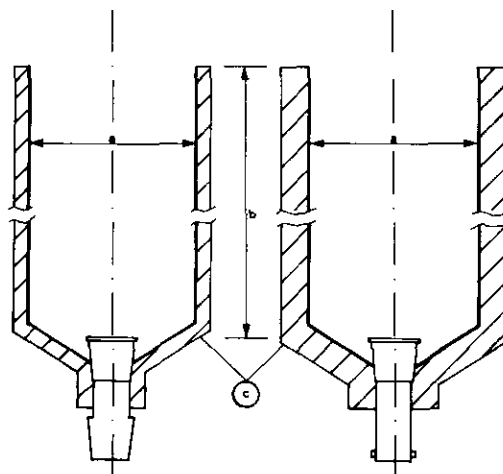


FIGURE 5. Cryo vessels: (left) dry ice/ethanol; (right) liquid nitrogen; (a) 120 mm; (b) 430 mm; (c) polyurethane foam.

in a water bath and equilibrium was reached throughout the whole system after approx 15-20 min. The volatilized compounds were further diluted with compressed air (10-15 L/min), and subsequently

introduced into a larger tube of Teflon (1000 × 60 mm diameter). This tube was connected to a centrifugal fan which created a flow of approx 1500 L/min. At the mixing point of the two streams, water vapor was introduced. Samples of generated mixtures were taken approximately 10 tunnel diameters from the mixing orifice. CO₂ was added to the sample stream after it was withdrawn from the dilution tube. This was done since then less CO₂ was needed, and the volume percent could easily be calculated by introducing a known flow of 100% CO₂ (NTP) into a comparatively small known sample flow taken from the dilution tube. First, the physical arrangement of the filling material in the condensers was optimized to obtain as large a sample amount as possible before clogging (ice and dry ice formation). By using different filling materials (glass rings and beads of different sizes) ca. a 1.5 m³ sample volume could be sampled at a maintained flow of 75 L/min (air saturated with water at 25 ° C and 7% CO₂).

This type of cryogenic trapping device will inevitably create aerosols in the sample stream. However, ice and dry ice formation in the last two condensers

enhances the trapping surface and thus prevents the aerosol from penetrating the system. This was confirmed in the following way. Cyclohexane (C-6) was mixed with dry air to 52 ppm in the laboratory dilution tunnel. A flow of 32 L/min of this mixture was sampled with a filter (held at -70 ° C) placed at the top of the sampling system, i.e., after the condensers. The concentration of C-6 found in the sample stream between the condenser immersed in liquid nitrogen and the filter was 6 ppm, while after passing through the filter it contained less than 0.5 ppm. This shows that C-6 formed fine particles and, in spite of the filling material, this aerosol could not be completely retained. When introducing water and CO₂ in the sample stream, as described previously, a rapid formation of ice and dry ice crystals takes place, and the efficiency increases. However, before this larger surface area has been built up,

lower efficiency can be encountered during the first seconds at real sampling.

Subsequently, other trace components of different volatility were generated in the dilution tube and the trapping efficiency was calculated (Table 1). These breakthrough studies were performed by means of gas chromatography-FID with a heated loop injector. All these experiments were performed with an entrance temperature of 25 ° C which gave exit condenser temperatures of +8°C, -55°C and -155°C, respective. However, the temperature within the liquid nitrogen condenser indicated the possibility of trapping NO. This gas is prevalent in automobile exhausts and has a freezing point of -164°C. In order to investigate if NO was enriched, a 200 ppm sample stream was generated. The trapping of NO was not quantified, but after disassembling the liquid nitrogen condenser, NO was observed as a bright blue solid.

Vehicle Test Procedure

The test vehicles, gasoline 2.1 L and diesel 2.3 L, were driven on a chassis dynamometer according to FTP-72. Diluted gas was sampled in a dilution tunnel (0.25 × 4.6 m) connected to a Horiba constant volume sampler. The approximate dilution ratio in these tests were 1:10 (gasoline) and 1:7 (diesel), giving a residence time of ca. 1 sec.

Extraction and Analyses

Filters (Gelman A/E glass fiber and Pallflex T60A20 Teflon-coated) were washed in ethanol and heated for 1 hr at 120°C before sampling. After sampling they were extracted with dichloromethane for 24 hr. Siphoning time was 8 min, 60 mL volume. All condensers were extracted for 18 hr in a special Soxhlet apparatus (Fig. 6). Siphoning time was 30 min with an extraction volume of 750 mL (water condenser), 550 mL (CO₂ condenser) and 450 mL (nitrogen condenser), respectively. After completed extraction, the solvent was evaporated under reduced

Table 1. Trapping efficiency for artificial sample streams.

Compound	Flow, L/min	C _i , ppm ^a	Trapping, % ^b
n-Pentane	71.7 ± 0.6	52.3 ± 3.9	93 ± 4
	54.5 ± 0.6	78.2 ± 1.5	98 ± 1
Cyclohexane	70.6 ± 0.6	45.0 ± 9.1	97 ± 1
	34.5 ± 0.3	50.0 ± 2.7	98 ± 3
Chlorobenzene	74.4 ± 0.7	17.7 ± 3.5	99 ± 1
Isobutyric aldehyde	34.3 ± 0.3	46.6 ± 3.7	99 ± 1

^aInlet concentration, detection limit 0.5 ppm.

^b(1 - C/C_i)100, where C outlet concentration, three to five determinations.

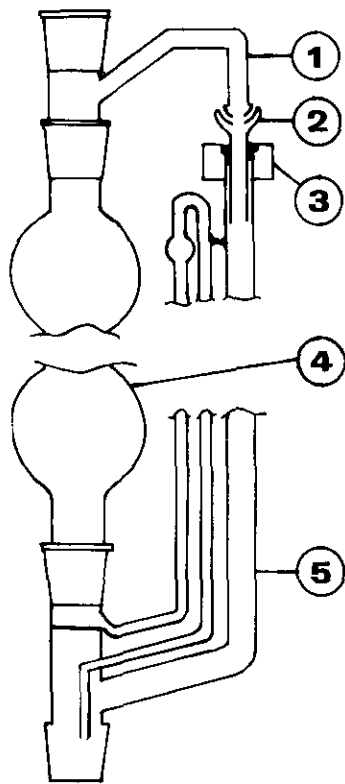


FIGURE 6. Soxhlet extractor for condensers: (1) vapor tube, upper part; (2) ball joint; (3) glass/Teflon seal with thread; (4) condenser; (5) vapor tube.

pressure. Clean-up was a simple liquid/liquid partition with dimethylformamide and water, as described elsewhere (8). Separation and quantitation with internal standards were performed by means of glass capillary gas chromatography and flame ionization detection. The gas chromatograph (PYE-Unicam GCV) was connected to a Spectra Physics 4100 computing integrator.

Identification by mass spectrometry was performed with a JEOL D-300 MS connected to a INCOS 2000 data acquisition system. Electron impact 70 eV and a scanning over 35–350 AMU/sec was used at a resolution of 700.

All solvents used were of analytical quality and redistilled in a 1.5 m all-glass column.

Results and Discussion

In the following we will discuss in more detail different parameters which have been investigated, and the specific problems involved with the use of this method. However, we will confine most of the discussion to the ice/water condenser and filter since

these two together trap PAH to more than 95%. Only small amounts of phenanthrene and anthracene will be found in the second condenser.

Extraction of Condensers

Gasoline exhausts contain about 10–12% of water which will condense in the first two condensers, yielding 5–50 mL, of which the most is precipitated in the first condenser. The collected water in this condenser (ice/water cooled) forms a slowly upwards moving front during sampling, but with the flow rates used, no breakthrough of liquid water has been observed. However, at 8°C which is the exit temperature of the sample stream from the ice/water condenser, the remaining water vapor content is still substantial and will eventually clog the dry ice/ethanol condenser by ice formation. The condenser cartridge immersed in liquid nitrogen will trap CO₂ and, as mentioned previously, NO/NO₂ from the exhausts. The formation of dry ice leads finally to the clogging of this condenser.

After sampling, each condenser is extracted, and the extracts obtained are analyzed separately. Three different solvents have been tested for the extraction: cyclohexane, (C-6), dichloromethane, (DCM), and acetone. C-6 and DCM are not miscible with water and thus give two phases during extraction. However, the number of experiments made using C-6 is small, and since C-6 has less ability to dissolve higher molecular weight PAH and oxidized polycyclics (14), we decided to discontinue the use of this solvent in favor of the more polar DCM. Acetone gives one phase, but on the other hand the remaining water must be reextracted after evaporation of the acetone. The extracts recovered from all the condensers are acidic (pH ~ 3) due to the trapping of organic acids and nitric/nitrous acids. Sulfuric acid, emanating from the sulfur in the fuel, especially diesel, is also a possible reason for the decrease in pH.

Due to the acidic property of these condensates a series of parallel sampling of diluted exhausts was performed to determine if pH had any effect on mutagenicity (15) or PAH recovery of the sample. For these tests only the ice/water condensers were used together with a filter.

Four test series were run (two gasoline and two diesel) with three sampling trains. The condensers were extracted with DCM together with three different buffers, pH 3, pH 7 and pH 11, respectively. The buffer, 75 mL, was added to the round-bottomed flask (Fig. 1) before sampling. After sampling, DCM was added, and the condensers were extracted for approx 18 hr. DCM has a higher density than water; thus, during boiling the two solvents are

constantly mixed. After completed extraction, the two phases were separated and the organic phase was reduced in volume by rotary evaporation. The sample was divided into two parts; 80% was used for mutagenicity tests and the remainder for chemical analysis.

No influence of the recovery of PAH was noted when different buffers were used during the extraction, but the organic background with use of acidic buffer was substantially higher in the gas chromatogram with FID, which made the interpretation of the analysis more difficult. However, extraction of the condensers with acetone after extraction with DCM (pH 7) showed that DCM did not yield a quantitative result of components more polar than PAH. Presumably, the reason for these results is that the condensed water on the glass beads/wall forms a layer which will prevent DCM to wet the total glass surface. Consequently, components which are dissolved in this water layer and/or adsorbed to the glass surface will not be extracted, and the possibility for "carry-over" between tests will also occur. Thus, these results show a limited applicability of this two-phase system.

Since these experiments showed difficulties in using a nonwater-soluble solvent for the extraction, we continued with a number of experiments with the use acetone, which has good ability to wet glass. However, acetone gives a "total" extract of both polar water-soluble and nonpolar species, which is why this acetone/water mixture will contain certain toxic components such as phenols. Thus, in order to investigate if a partition of such an extract influenced the total mutagenic effect, the following experiments were performed. The acetone extract was divided into three parts: to two of these, 50 mL of water or a corresponding amount of pH 7 buffer was added. After evaporation of the acetone phase, the extracts with added water and buffer respectively were further extracted with DCM (1×20 mL + 2×10 mL). Subsequently, the DCM was carefully evaporated to dryness and the residue dissolved in 5 mL acetone. The third extract was evaporated, and the remaining acidic water phase was used without any treatment. These three samples were tested for mutagenicity, and the results showed that the "total" extract exhibited more mutagenic activity (TA 100) than the corresponding DCM extracts. There was no difference between the acidic extract (only water added) and the neutralized extract. However, inconsistent results were obtained when trying to reproduce these tests with another vehicle. In these cases, no difference was indicated between a total extract and a neutralized which was further DCM extracted (15).

Artifact Formation Due to Nitrogen Oxides

Lately, extensive interest has been focused on the role of NO/NO₂ during sampling of particles. It has been shown that nitrated species can be formed under certain experimental conditions (16), and it has also been concluded that the possible formation of nitro-polycyclics is dependent on the filter material (17). The possibility for nitration during realistic filter sampling has been investigated. In one type of experiments, the NO₂ concentration was increased by altering the dilution ratio, or by adding NO₂ into the dilution tunnel. Mutagenicity was used as a quantitative tool and an increase was found at higher concentrations of NO₂ (18). Another type of experiment involves re-exposure of filters previously used. The results obtained with diesel exhausts showed that 6-nitrobenzo(a)pyrene and 1-nitropyrene were formed. The conversion ratio was not reported but an increase in the mutagenicity was found after 10 min exposure to particle-free diesel emissions (19). Formation of 1-nitropyrene have shown to have a decisive influence on the mutagenicity (20), since this component is a very strong mutagen. On the other hand, it is most likely that this component as well as other nitrated polycyclics are naturally abundant in diesel exhausts and some even in gasoline exhausts (21,22).

In sampling diluted automobile exhausts, the concentration of NO₂ is likely to be lower than 5 ppm in diesel exhausts and considerably lower in the case of gasoline. NO₂ is the reactive species, but it has also been concluded that if any nitration should occur at these sampling temperatures, NO₃ also must be present (16).

We have conducted a series of experiments with the addition of NO₂ prior to the filter. The samples were taken from a dilution tunnel and both filter and ice/water condenser were used. Two runs of both gasoline and diesel exhaust were performed and each sample consists of one reference plus two parallels with NO₂ added to 7.2 ± 0.4 and 24 ± 1 ppm, respectively. The condensers were extracted with DCM and buffer pH7 and the filter with DCM.

After extraction the samples were divided into two parts: one used for mutagenicity tests (80%) and the rest used for chemical analysis. The results of the mutagenicity tests are described elsewhere (15). Summarizing, the addition of NO₂ increases the mutagenic effect of the filter sample. The gas phase, however, did not show any increase in mutagenicity with the addition of NO₂, and this applies to both gasoline and diesel exhausts. These results were obtained with DCM extraction which limits

the conclusions. In spite of this, it is plausible to assume that any significant formation of 1-nitropyrene in the gas phase can be excluded, since such a component should have increased the mutagenic effect.

The addition of NO_2 to gasoline exhausts involves a degradation of cyclopenteno(cd)pyrene (Fig. 7) and BaP (Fig. 8) on the filter. This effect occurs already at 7 ppm NO_2 . We have had earlier experience with strongly fluctuating values of CPcdP when sampling undiluted exhausts (23), and it is feasible to believe that the NO_2 concentration in the exhausts could be one possible reason for this.

A decrease of BaP also occurred in sampling

diesel exhausts. Formation of 6-nitrobenzo(a)pyrene is possible (19), and work is under progress to confirm its presence. Nitroderivatives of CPcdP have, to our knowledge, not yet been reported.

In one series of experiments, with gasoline exhausts only, a comparison with different filter media was conducted. Either two filter holders were equipped with Teflon-coated filters (Pallflex T60A20) and one with a glass fiber filter (Gelman A/E) or vice versa. NO_2 , from the same tank as in earlier experiments, was added prior to the filter, and in three experiments either type of filter was used as reference (no NO_2 added). These results showed that on both types of filters degradation of CPcdP occurred when

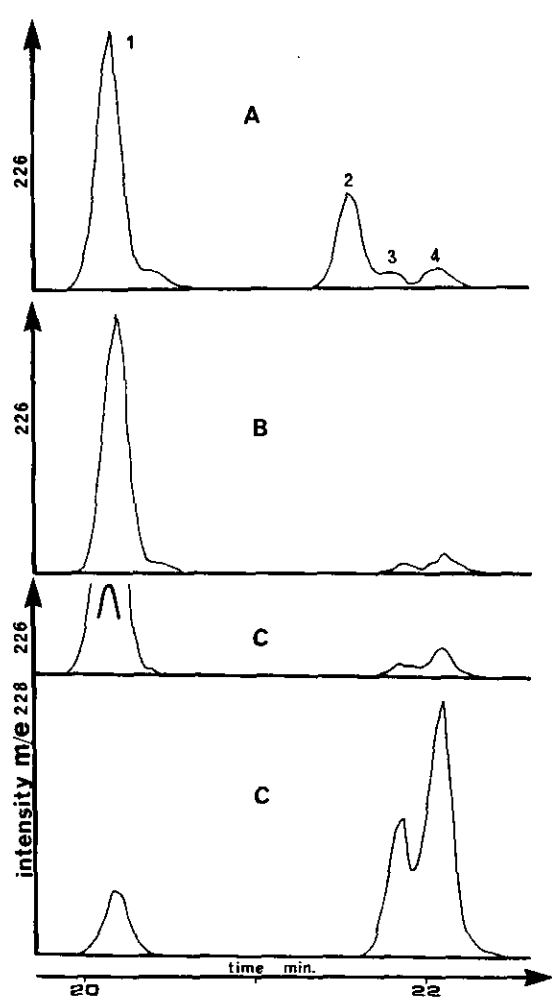


FIGURE 7. Mass chromatograms of ions m/e 226 and 228. Particulate sample from diluted gasoline exhausts. Three parallel sampling trains: (A) reference; (B) reference + 7 ppm NO_2 ; (C) reference + 24 ppm NO_2 . Peak assignments: (1) benzo(ghi)fluoranthene; (2) cyclopenteno(cd)pyrene; (3) benzo(a)anthracene; (4) chrysene.

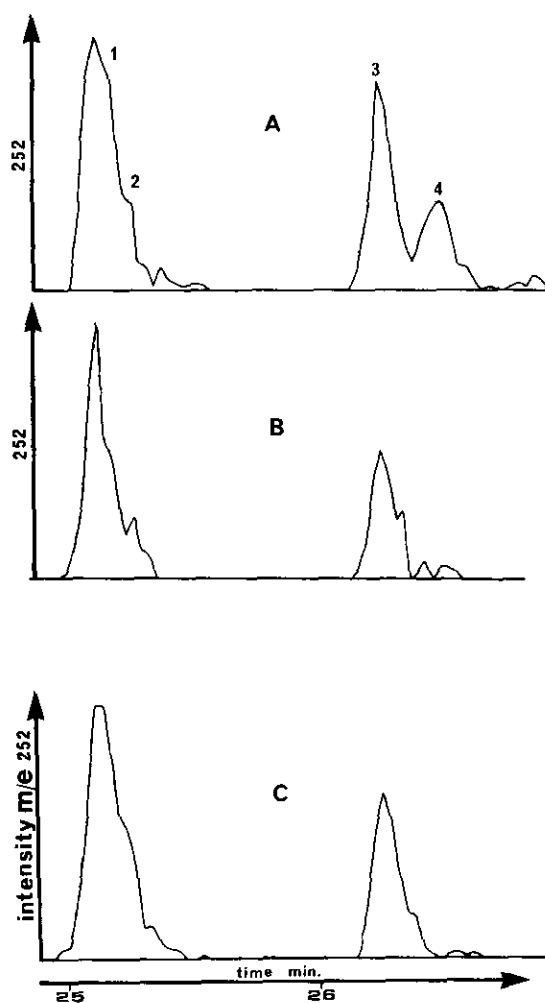


FIGURE 8. Mass chromatograms of ion m/e 252. Particulate sample from diluted gasoline exhausts. Three parallel sampling trains: (A) reference; (B) reference + 7 ppm NO_2 ; (C) reference + 24 ppm NO_2 . Peak assignments: (1) benzo(b)fluoranthene; (2) benzo(k)fluoranthene; (3) benzo(e)pyrene; (4) benzo(a)pyrene.

NO₂ was added to approx 3 ppm in the exhausts. However, the degradation of BaP was much lower in these experiments for both types of filters, compared to that previously described.

Formation of 1-nitropyrene has not been confirmed in this investigation of gasoline exhausts. However, it is necessary to emphasize that the detection limit for this component or other nitrated components is unfavorable, since split-splitless injection and not an on-column technique was used (21).

The addition of NO₂ to diesel exhausts involves a degradation of BaP, (only glass fiber filters used). CPcdP could not be detected at all in this emission, $\leq 0.1 \mu\text{g}/\text{km}$, probably due to a naturally high concentration of NO₂ in this type of emission. Comparing the amounts of PAH found with and without the addition of NO₂, there is an overall lower concentration of all when nitrogen oxide is added (Table 2). In the case of pyrene, approximately 30% less is found after addition of 24 ppm NO₂ to the exhausts. However, we were not able to distinguish any difference in the concentration of 1-nitropyrene between the reference filter and the filters to which NO₂ had been added. The amount found was low ($0.13 \mu\text{g}/\text{m}^3$) and was determined by MS/MID, monitoring of four ions. The NO₂-exposed filters also contained nitro derivatives of molecular weight 178, likely nitrophenanthrene, a compound not detected on the reference filter.

Trapping of Gas-Phase PAH

Gasoline Exhausts. As mentioned previously, earlier investigations have shown that certain PAHs < five rings) can be found in gas traps after a filter even when sampling diluted exhausts (10,11). Generally, the distribution of PAH between particles and gas phase is dependent on dilution ratio and sampling temperature; i.e., an increased dilution ratio leads to a lower temperature in the tunnel which increases the adsorption on particles, but on the other hand the residence time will be shorter which hampers the adsorption. The temperature on the filter varies during the cycle and has been typically between +20°C from start and up to +35°C at peak load in these tests. We have previously shown (12) that three- and four-ring PAHs are predominantly in the gas phase with a filter temperature of +45°C, and at this temperature it is also possible to detect five-ring PAHs, e.g., benzo(a)fluoranthene and benzo(a)pyrene and benzo(e)pyrene, in the gas phase.

A comparison between these earlier results and those obtained here shows that an approximate decrease of 10–15°C in filter temperature yields five-ring PAHs more than 99% particle-associated. Four-ring PAHs, such as benzo(a)anthracene, chrysene, cyclopenteno(cd)pyrene and benzo(ghi)fluor-

Table 2. PAH found on particulates from diluted diesel exhausts.^a

Component (FTP-72)	PAH, $\mu\text{g}/\text{km}$		
	Reference	7 ppm NO ₂	24 ppm NO ₂
Phenanthrene	50.2	51.1	47.2
Fluoranthene	136.9	124.0	103.5
Pyrene	105.4	76.2	70.8
Benzo(ghi)fluoranthene	35.0	28.9	24.5
Cyclopenteno(cd)pyrene	≤ 0.1	≤ 0.1	≤ 0.1
Benzo(a)anthracene	15.0	16.9	11.5
Chrysene	30.3	25.8	21.6
Benzo(b&k)fluoranthene	36.3	26.1	19.4
Benzo(e)pyrene and benzo(cd)pyrenone	22.6	19.8	13.3
Benzo(a)pyrene	5.2	0.1	0.1
Indeno(1,2,3-cd)pyrene	11.6	7.5	6.7
Benzo(ghi)perylene	16.5	7.9	9.2
Coronene	9.5	4.4	2.0

^aThree parallel sampling trains, two with NO₂ added prior to the filter.

anthene are 90–95% particle associated, compared to approximately 70% at the higher filter temperature. The difference is less pronounced for three-ring PAHs, such as phenanthrene and anthracene, of which more than 90% are in the gas phase at both temperatures. Pyrene is found in equal amounts in gas and particulate phase at -30°C filter temperature. However, high boiling PAHs, such as benzo(a)pyrene and coronene, will always be adsorbed on the particles, and this seems to be independent of dilution, since these components are particle-associated already in the tailpipe (12).

Diesel Exhausts. To our knowledge the occurrence of gas-phase PAHs in diesel exhausts has not been previously reported. In diluted diesel exhausts, approximately 50% of three-ring PAHs are in the gas phase at -2°C filter temperature. Four-ring PAHs, such as fluoranthene and pyrene, are to 5–10% in the gas phase, while PAHs of higher molecular weight are almost completely particle-associated. The ability to adsorb low molecular PAHs, i.e., three- and four-ring systems, is important when comparing the "total" PAH emission with gasoline and diesel exhausts. Since the latter adsorbs these substances to a large extent to the particulate emission, a filter sample only will be comparatively valid, but this is not the case with gasoline exhausts. Here, only a filter sample will lead to a significant underestimate.

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REFERENCES

1. Stenberg, U., Alsberg, T., and Westerholm, R. Emission of carcinogenic components with automobile exhausts. *Environ. Health Perspect.* 47: 53-63 (1983).
2. Stenberg, R. L., von Lehmden, D. J., and Hangebrauck, R. P. Sample collection techniques for combustion sources—benzopyrene determination. *Am. Ind. Hyg. Assoc. J.*, 22: 271-275 (1961).
3. Begeman, C. R., and Colucci, J. M. Apparatus for determining the contribution of the automobile to the benzene-soluble organics in air. National Cancer Inst. Monograph 9: 17-52 (1962).
4. Grimmer, G., Hildebrandt, A. and Böhnke, H. Sampling and analytics of polycyclic aromatic hydrocarbons in automobile exhaust gas: 1. Optimization of the collecting arrangements. *Zbl. Bakt. Hyg., I. Abt.* B158: 22-34 (1973).
5. Kraft, J., and Lies, K. H. Polycyclic aromatic hydrocarbons in the exhausts of gasoline and diesel vehicles. Society of Automotive Engineers, Warrendale, PA, 1981, paper no. 810082.
6. Chipman, J. C., and Massey, M. T. Proportional sampling system for the collection of an integrated auto exhaust gas sample. *J. Air Pollut. Control Assoc.* 10: 60-69 (1960).
7. Spindt, R. S. First annual report, Polynuclear Aromatic Content of Heavy Duty Diesel Engine Exhausts Gases, Gulf Research and Development Co., CAPE-24-72, July 1974.
8. Stenberg, U., Alsberg, T., and Bertilsson, B. M. A comparison of the emission of polynuclear aromatic hydrocarbons from automobiles using gasoline or a methanol/gasoline blend. Society of Automotive Engineers, Warrendale, PA, 1981, paper no. 810441.
9. Hare, C. T., Springer, K. J., and Bradow, R. L. Fuel and additive effects on diesel particulate-development and demonstration of methodology. Society of Automotive Engineers, Warrendale, PA, 1980, Paper no. 760130.
10. Pedersen, P. S., Ingversen, J., Nielsen, T., and Larsen, E. Effects of fuel, lubricant and engine operating parameters on the emission of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* 14: 71-79 (1980).
11. Lee, F. S.-C., Prater, T. J. and Ferris, F. PAH emission from a stratified-charge vehicle with and without oxidation catalyst: sampling and analysis evaluation. In: *Polynuclear Aromatic Hydrocarbons*, P. W. Jones and P. Leber (Eds.), Ann Arbor Science Press, Ann Arbor, MI, 1979, pp. 83-110.
12. Stenberg, U., Westerholm, R., Alsberg, T., Rannug, U., and Sundvall, A. Enrichment of PAH and PAH derivatives from automobile exhausts, by means of a cryo gradient sampling system. Paper presented at 6th International Symposium on PAH. Columbus, OH, Oct. 23-27, 1981.
13. Handa, T., Yamamura, T., Kato, Y., Saito, S., and Ishii, T. Determination of average emission rates of polynuclear aromatic hydrocarbons from an automobile. *J. Japan. Soc. Air Pollut.* 14: 98-105 (1979).
14. Stenberg, U., and Alsberg, T. Vacuum sublimation and solvent extraction of polycyclic aromatic compounds adsorbed on carbonaceous materials. *Anal. Chem.* 53: 2067-2072 (1981).
15. Rannug, U., Sundvall, A., Westerholm, R., Alsberg, T., and Stenberg, U. Paper presented at EPA Symposium on Application of Short-Term Bioassays in the Analysis of Complex Environmental Mixtures, Chapel Hill, NC, January 25-27, 1982.
16. Pitts, J. N., Jr., van Cauwenberghe, K. A., Grosjean, D., Schmid, J. P., Fitz, D. R., Belser, W. L., Knudson, G. B., and Hynds, P. M. Atmospheric reactions of polycyclic aromatic hydrocarbons: facile formation of mutagenic nitro derivatives. *Science* 202: 515-519 (1978).
17. Lee, F. S.-C., Pierson, W. R. and Ezike, J. The problem of PAH degradation during filter collection of airborne particulates—an evaluation of several commonly used filter media. In: *Polynuclear Aromatic Hydrocarbons*, A. Björseth and A. J. Dennis (Eds.), Battelle Press, Columbus, OH, 1980, pp. 543-563.
18. Bradow, R. L. Diesel particle emissions. *Bull. N.Y. Acad. Med.* 56: 797-811 (1980).
19. Gibson, T. L., Ricci, A. I., and Williams, R. L. Measurements of polynuclear aromatic hydrocarbons, their derivatives, and their reactivity in diesel automobile exhausts. In: *Polynuclear Aromatic Hydrocarbons*, M. Cooke and A. J. Dennis (Eds.), Battelle Press, Columbus, OH, 1981, pp. 707-717.
20. Salmeen, I., Duirisin, A. M., Prater, T. J., Riley, T., and Schuetzle, D. Contribution of 1-nitropyrene to direct acting Ames assay mutagenicities of diesel particulate extracts. *Mutat. Res.* 104: 17-23 (1982).
21. Schuetzle, D., Riley, T., Prater, T. J., Harvey, T. M., and Hunt, D. F. The identification of nitrated derivatives of PAH in diesel particulates. *Anal. Chem.* 54: 265-271 (1982).
22. Nishioka, M. G., Petersen, B. A., and Lewtas, J. Comparison of nitro-aromatic content and direct-acting mutagenicity of diesel emissions. Paper presented at 6th International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, OH, Oct. 27-29, 1981.
23. Stenberg, U. Emission of polynuclear aromatic hydrocarbons from gasoline vehicles. Report to the Swedish EPA, February 1, 1979.