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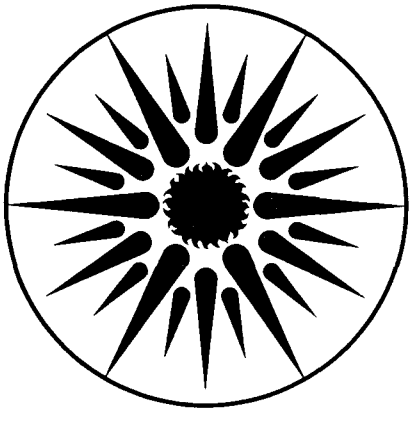

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SEMI-VOLATILE AND PARTICULATE POLYCYCLIC AROMATIC HYDROCARBONS IN ENVIRONMENTAL TOBACCO SMOKE: CLEANUP, SPECIATION AND EMISSION FACTORS

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ABSTRACT

Studies of phase distributions and emission factors for polycyclic aromatic hydrocarbons (PAH) in environmental tobacco smoke (ETS) require collection and analysis of very small samples. To achieve the necessary selectivity and sensitivity, a method has been devised and tested for extraction and cleanup of gas- and particulate-phase ETS samples. Gas-phase species were trapped by polymeric sorbents, and particles were trapped on filters. The samples were extracted with hot cyclohexane, concentrated and passed through silica solid-phase extraction columns for cleanup. After solvent change, the PAH were determined by high performance liquid chromatography with two programmed fluorescence detectors. PAH concentrations in 15-mg aliquots of National Institute of Standards and Technology Standard Reference Material SRM 1649 (Urban Dust/Organics) agreed well with published values. Relative precision at the 95% confidence level was 8% for SRM 1649 and 20% for replicate samples (5 mg) of ETS particles. Emission factors have been measured for a range of gas- and particulate-phase polycyclic aromatic hydrocarbons in ETS. The emission factors per cigarette were 13.0±0.5 mg particulate matter, 11.2±0.9 μg for gas-phase naphthalene and 74±10 ng for particulate benzo(a)pyrene.

KEYWORDS

sample cleanup, emission factors, environmental tobacco smoke, ETS, indoor air, polycyclic aromatic hydrocarbons, PAH, phase distribution, silica, solid phase extraction

INTRODUCTION

Despite their importance as carcinogens in indoor air, concentrations of polycyclic aromatic hydrocarbons (PAH) in environmental tobacco smoke (ETS) have rarely been measured *(1-3)*. Furthermore, measurements of ETS concentrations in a single setting cannot be used to extrapolate concentrations for other indoor settings unless the air exchange rate has also been measured. However, emission factors can be used to predict indoor concentrations of pollutants when ventilation rate data is incorporated into time-dependent mass balance equations *(4)*. To our knowledge, no measurements of emission factors (mass cig^{-1}) have been reported for ETS. Although emission factors have been determined recently for a range of PAH in mainstream (MS) and sidestream smoke (SS) *(5, 6)*, their phase distributions and relative proportions in ETS have been the subject of very little work.

Both the size of the sample that can be collected in indoor environments and the chemical complexity of ETS have hampered efforts to study the PAH. For indoor air sampling, the flow rate must be significantly less than the ventilation rate to minimize the impact of sampling on measured concentrations. For example, in a 25 m^3 room, a sample flow rate of 34 L min^{-1} is equivalent to a ventilation rate of 0.082 hr^{-1} and can reduce the indoor concentration by 17% over a 12-hour sampling period when the air exchange rate is 0.3 per hour *(7)*. Using these sampling conditions in a home with a smoker yielded only 5 mg of particles *(8)*. The corresponding gas phase PAH could be analyzed by gas chromatography with mass-spectrometric detection (GC-MS), but determination of the particulate PAH in that small sample required a technique with higher analytical sensitivity. In addition, for phase distribution studies, the semi-volatile PAH in gas-phase ETS must be determined over a concentration range of four orders of magnitude in a single sample.

GC-MS has been used successfully to determine gas- and particulate-phase PAH in ETS *(1, 2)*, but detection limits required air sample volumes greater than 100 m^3. A recent study of ETS in a large public facility collected PAH from about 6000 m^3 of (sampled) air *(3)*. For most indoor air environments, a more sensitive method is clearly needed. High performance liquid chromatography with fluorescence detection (HPLC-FD) can meet the sensitivity requirements for samples collected in residences. However, the complex chemical nature of ETS presents analytical problems. When no sample cleanup was used for particulate ETS samples *(8-10)*, determination of PAH by HPLC-FD was complicated by the presence of interferences and high background.

Early cleanup and isolation methods for PAH in tobacco smoke used at least 100 cigarettes per extract and relied on liquid-liquid extraction and large column fractionation *(11, 12)*. A widely-cited analytical method for PAH in tobacco smoke requires all the mainstream smoke particles from at least four cigarettes *(13)*. During the last decade, progressively simpler cleanup procedures have been developed to isolate the PAH in MS and SS particles before determination by HPLC-FD, but relatively large samples were still required *(5, 14, 15)*.

The objectives of this investigation were to develop cleanup and detection methods suitable for both gas- and particulate-phase PAH in small samples of ETS, and to use the methods to measure emission factors and phase distributions for PAH in ETS. Evaluation criteria for the cleanup method were (1) good recoveries of PAH from the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1649 Urban Dust/Organics, (2) good accuracy and relative precision of measurements for SRM 1649 particles, and (3) good relative precision of measurements for both the gas and particulate phases of ETS. Emission factors were determined under controlled conditions in an environmental chamber using simulated ETS. A time-dependent mass balance model *(4)* was used to calculate emission factors from measured concentrations, environmental chamber volume and air exchange rates.

EXPERIMENTAL DETAILS

Materials. Standard PAH were obtained from Aldrich Chemical Co. and the NIST and used without further purification. Deuterated fluoranthene and phenanthrene were obtained through the National Repository Service of the National Cancer Institute. HPLC-grade solvents were obtained from Burdick and Jackson, Inc. Solid phase extraction columns were obtained from the following suppliers: silica, C_8 and C_{18} Sep-Paks from the Waters Inc.; and cyanopropyl-bonded silica from J.T. Baker, Inc. Before use the SPE columns were washed with 6 mL each of the following solvents in this order and air dried: hexane, ethyl acetate, methylene chloride and

methanol. An alternate cleanup procedure was adopted for routine use of the Waters silica SPE columns, in which 6 mL of each of these solvents was passed through the SPE column in this order: cyclohexane, methylene chloride and acetonitrile. (Fluorescent impurities were observed if the wash order was reversed.) In addition, hand-packed silica SPE columns (containing 200 or 500 mg of microporous silica obtained from Waters) were assembled from 5-mL glass syringe barrels and cleaned with cyclohexane, methylene chloride and acetonitrile. Pre-heated (800 °C) quartz fiber filter disks (Pallflex Corp.) were used to contain the silica bed in the syringe barrels. Commercially available silica Inert-SPE® columns from Burdick and Jackson Laboratories were also found to be acceptable.

Collection of ETS. For method development, commercially available filter-tipped cigarettes were machine-smoked in environmental chambers (27 and 36 m^3). Single-port and 12-port smoking machines used a puff rate of 2 min^{-1} and puff volume of 35 mL. ETS was simulated by mixing the emitted side stream smoke throughout the chamber with fans. ETS was sampled at 20 L min^{-1} through pre-extracted (in dichloromethane and methanol) Teflon-coated 47-mm diameter glass-fiber filters followed by sorbent beds containing 2.5 mg of XAD-4 precleaned resin with mesh size range of 20-60 (Alltech Associates, Inc.). After receipt, the XAD had been further cleaned by Soxhlet extraction for eight hours each with dichloromethane and methanol and then dried with warm (60 °C) N_2 in a fluidized bed for eight hours. After sample collection the filters and sorbent beds were stored separately at -20 °C. For the emission factor studies, ETS from Kentucky Reference cigarettes (1R4F) was collected using the annular denuder-based Integrated Organic Vapor-Particle Sampler (IOVPS) *(16)* in the 36 m^3 chamber. Extraction procedures for the denuders (for gas-phase PAH) and filters (for particulate-phase PAH) are described in reference 16. The chamber air exchange rate was measured during the ETS sampling period by a tracer gas technique using SF_6 *(17)*. After injection of the tracer its concentration was monitored every few minutes by gas chromatography.

Extraction solvents for ETS. Identical composite filter samples, 2.0 mg each, were prepared from archived samples of ETS collected in an earlier study *(8-10)*. These were extracted using several solvents for comparison of extraction efficiencies and cleanup methods. Cyclohexane, n-hexane, dichloromethane, acetonitrile and a benzene-methanol (1:1, v:v) mixture were compared using sonication at room temperature for 15 min.

Column comparison. SPE columns that were used in the normal-phase mode (silica and cyanopropyl) were wetted with n-hexane before application of a standard mixture. A methanol-water mixture (3:7, v:v) was used to condition the reversed-phase columns (C_8, C_{18} and cyanopropyl). A 200-µliter aliquot of a PAH standard mixture was applied to each column. The amounts of PAH added to each column were fluoranthene, 31 ng; pyrene, 33 ng; benz(a)anthracene, 15 ng; chrysene, 14 ng; benzo(e)pyrene, 53 ng; benzo(b)fluoranthene, 16 ng; benzo(k)fluoranthene, 18 ng; benzo(a)pyrene, 19 ng; benzo(ghi)perylene, 30 ng; and indeno(1,2,3-cd)pyrene, 33 ng. The normal-phase SPE columns were eluted with 4 mL of a mixture of dichloromethane and hexane (1:3, v:v), and the eluate was rotary-evaporated to around 200 µL. The reversed-phase SPE columns were eluted first with 2 mL of the methanol-water mixture that was discarded. The second wash with 2 mL of acetonitrile was concentrated to 200 µL and analyzed.

HPLC analysis. The dual-detector wavelength-programmable fluorescence HPLC method for particulate PAH is described in detail elsewhere *(18)*. A Vydac 201TP5215 microbore column (15 cm in length and 0.21 cm id) was connected to a Hewlett-Packard HP1090M Solvent

Delivery System with two Hewlett-Packard Model 1046A detectors in series. ChemStation software controlled data acquisition and analysis. A 5 µL injection loop was used in a Rheodyne Model 8125 injector. Reversed-phase gradient elution used water, acetonitrile and tetrahydrofuran in an hour-long program.

For semi-volatile PAH from naphthalene to chrysene, analyzed from either the gas or particle phases of ETS, the dual-detector technique of Mahanama *et al. (18)* was modified as follows: The gradient program increased the eluant strength in a concave pattern from 38% acetonitrile, 2% THF, 60% water, to 95 % acetonitrile, 5% THF, over 39 min at 0.4 mL min^{-1}. The concave gradient rose steeply in strength from 32 to 40 min while the flow rate changed linearly from 0.4 to 0.5, and from 0.5 to 1 mL min^{-1} between 25.1 and 25.3, and 25.3 and 46 min, respectively. From 46 to 49 minutes the flow decreased linearly to 0.5 mL min^{-1}. The mobile phase composition returned to the initial condition between 48 and 50 min. A 15-minute equilibration at 0.5 mL min^{-1} followed. The column was maintained at 30.8 °C.

Each fluorescence detector was independently programmed to change excitation and emission wavelengths for selective detection of the semi-volatile PAH of interest as they eluted from the column. One detector started at excitation and emission wavelengths of 220 and 348 nm, respectively, to detect naphthalene and its 1- and 2-methyl derivatives, acenaphthene and acenapthylene. At 15.9 min it switched to 244 and 391 nm to detect phenanthrene and anthracene. At 23 min it changed to 232 and 423 nm to detect fluoranthene, its alkyl derivatives and pyrene and to minimize interference from methyl phenanthrenes. From 28.9 to 34.8 min the detector was set at 234 and 383 nm to detect alkyl pyrenes. At 34.8 min the settings changed to 288 and 405 nm to select benz(a)anthracene and its alkyl derivatives. The second detector started at 246 and 296 nm to detect biphenyl and fluorene; at 16.1 min it switched to 245 and 359 nm to detect phenanthrene and its alkyl derivatives; and at 34.9 min it switched to 263 and 371 nm to detect chrysene and its alkyl derivatives. These fluorescence programs were developed initially by studying the excitation and emission spectra of standard compounds to select conditions of both high sensitivity and selectivity *(18)*. However, the programs were modified to overcome interferences from other PAH and their alkyl derivatives in ETS extracts.

Determination of recoveries and precision for SRM 1649. During method development 5 mg samples of SRM 1649 were used routinely. The extraction and cleanup procedures were tested on 6 aliquots (15 mg each) of SRM 1649. The PAH content of this urban particulate material has been certified by the supplier. These samples were sonicated at 70 °C for 30 min in 7.5 mL cyclohexane, filtered and re-extracted in 7.5 mL fresh solvent under the same conditions. The filtered extracts were combined and passed through Waters "classic" silica (690 mg) Sep-Paks, concentrated to around 0.6 mL and diluted five-fold with an acetonitrile-tetrahydrofuran mixture (3:1,v:v) before HPLC analysis on the same day as they were prepared; otherwise degradation of the PAH was observed. For studies with ETS, the cyclohexane extract was reduced in volume by rotary evaporation before this step, as described below.

Precision of Analysis for PAH in ETS particles. For analytical precision studies with ETS particles, four samples were collected on clean Teflon-coated glass fiber filters (47 mm diameter) using two identical sampling lines (20 L min^{-1}) from two two-hour episodes of cigarette smoking in the 27 m^3 chamber. Six cigarettes were machine-smoked in each experiment. The average total suspended particle concentration was 1.7 mg m^{-3}, based on the net loading of the filters. Filter mass measurements were made with a Cahn Model 25 electrobalance. Each filter was cut into quarters, and four filter composites were prepared, each containing one quarter of each filter. Before extraction the total mass was determined for each composite (about 5 mg each). Each

composite filter sample was extracted by sonication for 15 min using 10 mL cyclohexane at 70 °C. Deuterated fluoranthene, added at the time of extraction, was used as the internal standard for recovery. After filtration of the first extract, the filter composite was extracted in a second 10 mL aliquot of cyclohexane. The two extracts were combined and concentrated to about 1 mL using a rotary evaporator, loaded onto a "classic" Waters silica (690 mg) Sep-Pak, and flushed with cyclohexane. The total volume of cyclohexane added to the Sep-Pak was 5.0 mL. Larger elution volumes were found to contain fluorescent interferences. The eluate was concentrated to about 1 mL, loaded onto a second clean Sep-Pak, and air dried overnight before elution with 5 mL acetonitrile. The final eluate was concentrated to between 0.5 and 1.0 mL before HPLC analysis. One of the composite extracts was lost during preparation.

Standard addition to ETS extract. One of the composite extracts of ETS from the precision study was used for the preparation of six aliquots, each of which was spiked with a standard mixture at a different concentration. The added concentration varied from none to about five times the concentrations observed in the unspiked diluted extract. Phenanthrene, fluoranthene, chrysene and benzo(a)pyrene were used as the standard compounds. The slopes and intercepts of the plots of added concentration versus detector response were used to calculate the concentrations of these PAH in ETS. The values were compared to the corresponding means for the replicates.

Semi-volatile PAH collected from the gas and particulate phases of ETS. Cleanup techniques for gas-phase semi-volatile PAH in ETS were modified versions of the procedures described above. The gas-phase components were adsorbed on XAD-4 resin beds or onto resin-coated annular denuders *(16)* of the IOVPS. The sorbent beds and annular diffusion denuders were extracted twice each by sonication with 15-mL aliquots of cyclohexane at 50 °C. Filter samples (with net ETS particle mass of 0.3 mg), collected by the IOVPS from one-hour sampling at 5 L min^{-1}, were extracted as described above. The extracts were reduced in volume to about 1 mL and added to lab-prepared SPE columns that contained 500 mg of microporous silica. A total of 5 mL cyclohexane passed through the column. For solvent change without evaporative loss of semi-volatile PAH or excessive dilution of the extract, the cyclohexane eluate was reduced in volume to between 0.3 and 0.5 mL and carefully added to a second lab-prepared SPE column that contained 200 mg silica. The top of the silica bed was exposed. The column was allowed to dry at room temperature in the dark. After about one hour, the SPE column was tapped to loosen the silica and carefully placed horizontally to dry. After three to four hours the silica was eluted with 2.0 mL acetonitrile. The eluate was evaporated to 0.5 mL and analyzed by HPLC. Both deuterated phenanthrene and deuterated fluoranthene, added at the time of extraction, were used as internal standards for recovery.

RESULTS

Development of the cleanup method for ETS

Figure 1a illustrates the problems encountered with fluorescence detection of PAH in dichloromethane or benzene-methanol extracts of ETS that were not subjected to cleanup *(8)* or wavelength-selective detection. Individual PAH peaks appeared as a fringe atop a high background of unresolved fluorescence, and signals from semi-volatile PAH at short retention times (naphthalene through chrysene) were obscured by large interferences from other, probably more polar, species. These features were also seen in indoor samples containing wood smoke particles *(8)*, but not in outdoor particulate matter or SRM 1649 samples. Use of dichloromethane extracts also led to peak distortion in reversed phase HPLC with acetonitrile

and water. Wavelength-selective emission and detection improved resolution somewhat, but the interferences were not eliminated.

To avoid these kinds of problems without introducing many additional preparation steps, small chromatographic SPE columns packed with silica were evaluated, along with three chemically-bonded silica materials, for their suitability in cleanup of ETS samples for HPLC-FD analysis. As a first step in developing the method, retention and recovery were evaluated for standard mixtures of PAH that were applied to several solid-phase extraction columns: normal phase silica and cyanopropyl-bonded silica, and reversed-phase C_{8}, C_{18} and cyanopropyl-bonded silica. Amino-bonded silica was not evaluated. Column eluates were subjected to HPLC with fluorescence detection *(18)*. Table 1 lists recovery data for each of ten PAH. Recovery of PAH from both reversed-phase SPE columns proved difficult, and the added water was difficult to evaporate. The amounts of non-polar solvent required to remove the PAH also removed fluorescing impurities from the SPE cartridge case. Non-bonded silica did not retain the PAH from acetonitrile, dichloromethane, hexane or cyclohexane solutions, and it proved superior to the cyanopropyl-bonded silica in trapping polar interferences from ETS extracts.

The high (137%) recovery of pyrene (Table 1) from the silica SPE column included a contribution of fluorescent material from the plastic case. The elution schemes used for the SPE column comparison did not include a cartridge blank, so correction for this effect was not possible. However, subsequent analysis showed that, even after extensive solvent rinsing, the plastic SPE case could contribute fluorescent materials that interfered with analysis for naphthalene, methyl-naphthalenes, phenanthrene, fluoranthene, pyrene and sometimes chrysene. The other PAH were not influenced. This problem was eliminated by using lab-made SPE cartridges in glass barrels.

In developing a cleanup method for ETS, extraction efficiency, solvent compatibility and solvent volatility must be optimized. Table 2 compares the overall extraction suitability of various solvents for PAH in ETS. Removal of fluorescing interferences and reduction of the fluorescing background from ETS were accomplished by a combination of solvent choice and silica cleanup. Cyclohexane, hexane, dichloromethane and a benzene-methanol mixture were compared. Of these, cyclohexane proved to be the best choice. Cyclohexane extracted PAH with less accompanying polar material than did dichloromethane, a solvent which is used frequently for PAH extraction from ambient air particulate matter. Silica cleanup of dichloromethane extracts did not remove enough of the interferences. Hexane removed fewer interferences than cyclohexane but it had lower extraction efficiency for PAH than cyclohexane. The benzene-methanol mixture was an excellent solvent system for PAH extraction, but it also dissolved sufficient polar ETS components to prevent cleanup with any of the tested SPE materials.

Acceptable chromatograms such as shown in Fig. 1b resulted from the sample cleanup scheme diagrammed in Figure 2. This is the recommended method for cleanup of particulate samples of ETS or airborne particles. Cyclohexane extracts of ETS from 47-mm filters were evaporated to 1 mL, passed through commercially available silica SPE (Sep-Pak) columns before evaporation to around 200 µL and subsequently diluted with tetrahydrofuran and acetonitrile to around 1 mL (1:1:3, v:v:v, for compatibility with reverse-phase HPLC in acetonitrile and water). A more concentrated extract could be prepared by drying the cleaned cyclohexane extract on a second silica SPE column and eluting with acetonitrile for subsequent evaporation to around 500 µL. Both procedures are designed to ensure (sample) solvent and HPLC mobile phase compatibility while controlling loss of the more volatile components of the extract. Fluoranthene-D_{10} was used

as an internal standard for losses of PAH during the workup. Its overall recovery in extraction of 30 filter samples ranged from 60 to 80%.

After the cleanup technique was developed for particulate PAH in ETS, it was modified for analysis of semi-volatile PAH collected from the gas and particle phases of ETS. The cleanup procedure was performed with laboratory-prepared silica SPE columns to minimize fluorescent interferences, as discussed above. A second more volatile internal standard, phenanthrene-D_{10}, was added at the time of extraction. The recoveries of the two internal standards were usually within 2% of each other and averaged 70%. PAH concentrations were normalized for recovery using the average recovery for the two standards.

Determination of PAH in NIST SRM 1649 and ETS

Table 3 shows the concentrations of particulate PAH in SRM-1649, urban dust/organics. Six 15 mg aliquots were extracted and cleaned up using the procedures described above. HPLC analysis used the dual-detector wavelength-programmed selective fluorescence method *(18)*. The value for phenanthrene is suspect because of interfering material due to the large volume of cyclohexane that passed through the column. After these experiments, the standard operating procedure was modified to reduce the extract volume before passage through the SPE column, and the phenanthrene interference decreased substantially. For the nine other compounds for which there are data available from NIST, the PAH concentrations averaged 98 $\pm$ 13 % of the published values. The relative precision averaged 8%. Fig. 3 shows the dual-detector chromatograms for one of the SRM 1649 samples. With the exception of phenanthrene, the results are in good agreement with the values reported by NIST, particularly in view of the 15 mg sample size extracted here. The published NIST values were determined from extracts of one gram sized samples.

Fig. 4 shows a chromatogram of an ETS extract from a filter loaded with a total mass of 2.6 mg particles. Using the fluorescence programs and peak height ratio data given by Mahanama *et al., (18),* PAH were determined in ETS from four identical (composited) filter samples with net particle mass of 5.0 mg each. Concentrations of nine PAH are given in Table 4 for the composited samples. The average relative precision at the 95% confidence level was 20%. To check the effect of the ETS matrix on quantification of PAH, standard addition experiments were performed. For all compounds added (phenanthrene, fluoranthene, chrysene and benzo(a)pyrene), the measured PAH concentrations were linearly dependent on added PAH with $r^2 = 0.99$. The slopes and y-intercepts of plots of response vs amount added led to calculated ETS concentrations that were within the experimental uncertainties of the PAH concentrations measured in the precision study. The results show that quantitation of particulate PAH is possible even in the presence of the unresolved fluorescent material seen in Fig. 4.

Fig. 5 shows dual-detector fluorescence chromatograms of the cyclohexane extract of semi-volatile gas phase ETS collected on an XAD-4 sorbent bed that was placed downstream of a filter. After 3 cigarettes were machine-smoked in a sealed 20 m^3 chamber, 0.7 m^3 of the chamber air passed through the sampler. The filter had 0.6 mg particles. The extract was cleaned up using lab-made silica SPE columns. Good peak separations were obtained, and peak height ratios of the PAH at two different sets of excitation and emission wavelengths were in good agreement with those of the standards. Table 5 shows the reproducibility of gas phase PAH concentrations as measured using a pair of co-located IOVPS *(16)* during the same chamber experiment. The IOVPS operated at half the flow rate of the sorbent bed sampler. The coefficients of variation (CV) were calculated from the estimated standard deviations for pairs

(19). The CV averaged 17% for the 12 gas-phase semi-volatile PAH. That number includes the sampling variability. PAH were determined in the corresponding particle-laden filters that had an average mass of 0.3 mg. For the semi-volatile PAH fluoranthene, pyrene, benz(a)anthracene and chrysene, the coefficient of variation averaged 9% in the particles.

Emission factors for PAH in ETS

The time-dependent mass balance model for a well-mixed chamber applied by Traynor, *et al. (4)* has been used to calculate emission factors for ETS. Emission factors are generally more useful than concentration data alone because they can be used to predict concentrations in a variety of settings with different smoking patterns, ventilation rates and room volumes. Emission factors were calculated from concentration data obtained in the 36 m^3 chamber using the equation:

$$E = Cva(dt) / n(e^{-at_i} - e^{-at_f})$$

where E is the emission factor in ng cig^{-1}, C is the concentration in ng m^{-3}, a is the air exchange rate in hr^{-1} including air removal by sampling, v is the chamber volume in m^3, t_i is the time (in hr after smoking cessation) sampling started, t_f is the time sampling ended, dt is t_f-t_i and n is the number of cigarettes smoked. The measured total suspended particulate mass concentration of 0.96 ± 0.03 mg m^{-3} led to an emission factor of 13.0 ± 0.5 mg of particulate matter cig^{-1} when wall deposition of particles was neglected. Wall deposition of respirable particles in a similar chamber was found to be less than 0.01 hr^{-1} by Offermann, *et al. (20).* PAH emission factors calculated from the concentration data of Table 5 are presented in Tables 6 and 7 for the gas and particulate phases of simulated ETS, respectively. The uncertainties were estimated by propagation of errors in each of the experimental parameters. Emission factors, determined by Evans *et al. (6)* for three of the same particulate PAH in SS from 1R4F reference cigarettes (benzo(b)fluoranthene, benzo(k)fluoranthene and BaP), and included in Table 7 for comparison, show good agreement with the measurements reported here. Using the data of Table 6 with a typical residential smoking pattern *(21)* in a time-dependent indoor air quality model *(4)* leads to a 24-hour average indoor naphthalene concentration of 36 ng m^{-3}.

SUMMARY AND CONCLUSIONS

To achieve the necessary selectivity and sensitivity for determining PAH in small ETS samples without extensive fractionation, an analytical approach has been developed that relies on silica SPE columns for removal of fluorescent interferences from ETS extracts before HPLC-FD analysis. In contrast to the earlier studies with MS and SS which focused primarily on BaP, a wide range of PAH can now be determined in both the gas and particulate phases of ETS. That has become possible due to the enhanced selectivity for PAH available with a recently-reported fluorescence technique *(18),* that uses two programmable detectors simultaneously, to identify unambiguously and quantitate PAH in extracts of ETS particles without extensive fractionation. In this study the dual-detector approach has been adapted for determination of both gas- and particulate-phase PAH in small samples of ETS.

Silica SPE cleanup of cyclohexane extracts of ETS substantially reduced amounts of fluorescing impurities so that determination of a wide range of semi-volatile and particulate PAH by HPLC was possible with good relative precision, even for samples as small as 0.3 mg particles obtained from sampling 0.3 m^3 air. PAH concentrations determined using the method agreed well with published values for standard reference material SRM-1649 urban dust/organics (airborne

particulate matter). The method has also been validated for semi-volatile PAH collected from both the gas- and particulate phases of ETS. Using a time-dependent mass balance model, emission factors have been calculated for PAH from their measured gas and particulate phase concentrations in simulated ETS.

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TABLES

FIGURE CAPTIONS

Figure 1. (a). Fluorescence chromatogram of a dichloromethane extract of 2 mg ETS particles [ref. 8] that had not been subjected to cleanup. Excitation at λ=250 nm with all emitted light with λ>305 nm collected. (b) Chromatogram of a cyclohexane extract of 2.6 mg simulated ETS from the environmental chamber that had been cleaned using silica SPE. Fluorescence conditions: 260 nm excitation and 375 nm emission. The tallest peak is due to chrysene.

Figure 2. Schematic diagram of the cleanup procedure for SPE cartridges with 500 and 690 mg silica. Abbreviations are Cx; cyclohexane; THF, tetrahydrofuran; and ACN, acetonitrile. The elution volume for the second (solvent change) SPE is 5 mL for 500 or 690 mg silica and 2 mL when 200 mg silica is used.

Figure 3. Chromatograms of NIST SRM 1649 urban dust/organics (15 mg particles). At these times, excitation and emission wavelengths, in nm, changed to: (a): 0 min, 250, 370; 11.5 min, 235, 380; 19.2 min, 225, 395; 22.7 min, 230, 390; 27.4 min, 290, 410; 30.2 min, 245, 480; (b): 0 min, 240, 390; 11.6 min, 230, 450; 19.4 min, 260, 370; 22.8 min, 230, 430; 30.4 min, 225, 415; 36.6 min, 290, 410. PAH abbreviations are Phen, phenanthrene; Pyr, pyrene; BaA, benz(a)anthracene; BeP, benzo(e)pyrene; BaP, benzo(a)pyrene; Ind, indeno(1,2,3-cd)pyrene; Fl-D_{10}, deuterated fluoranthene; Fl, fluoranthene; Chr, chrysene; BbF, benzo(b)fluoranthene; BkF, benzo(k)fluoranthene; and BghiP, benzo(ghi)perylene.

Figure 4. Chromatogram of a silica-cleaned cyclohexane extract of 2.6 mg ETS particles. The excitation and emission wavelengths were 245 and 443 nm, respectively. Abbreviations for PAH are defined in the caption of Fig. 3. Ant is the abbreviation for anthracene.

Figure 5 Dual-detector chromatograms of a silica-cleaned cyclohexane extract of the gas-phase semi-volatile PAH collected from 0.7 m^3 simulated ETS on an XAD-4 sorbent bed. The timetable for excitation and emission wavelength changes is given in the text. Abbreviations are Nap, naphthalene; 1-Me-nap, 1-methylnaphthalene; 2-Me-nap, 2-methylnaphthalene; acen, acenaphthene and acenaphthylene; Biph, biphenyl; Phen-D10, deuterated phenanthrene; 1-Me-phen, 1-methylphenanthrene; and 2-Me-phen, 2-methylphenanthrene. Other abbreviations are listed in the caption for Fig 3.

Table 1. Recovery of PAH from various SPE absorbents.

PAH	Mass Added ng	% Silica NP[a]	CN NP[a]	CN RP[b]	C_8 RP[b]	C_{18} RP[b]
Fluoranthene	31	89	67	41	35	16
Pyrene	33	137	89	66	21	nd[c]
Benz(a)anthracene	15	107	82	47	51	nd
Chrysene	14	107	76	47	54	nd
Benzo(e)pyrene	53	103	91	54	45	nd
Benzo(b)fluoranthene	16	111	94	50	43	nd
Benzo(k)fluoranthene	18	96	81	43	41	4
Benzo(a)pyrene	19	111	91	40	36	nd
Benzo(ghi)perylene	30	75	82	nd	nd	nd
Indeno(cd)pyrene	33	90	78	30	21	nd
Average		100	81	46	38	13

a. NP = normal phase.
b. RP = reversed phase.
c. nd = not detected.

Table 2. Suitability of various extraction solvents for determination of PAH in ETS.

Solvent	PAH Extractability	SPE Selectivity	HPLC Compatibility
Cyclohexane	good	excellent	poor
Hexane	mediocre	good	poor
Dichloromethane	good	polar interferences	poor
Benzene-methanol	excellent	polar interferences	mediocre
Acetonitrile	good	polar interferences	excellent

Table 3. Comparison of PAH concentrations in SRM 1649 with reference values.

PAH	Reference $\mu g\ g^{-1}$	Measured $\mu g\ g^{-1}$ [a]	n	CV % [b]	Prec % [c]
Phenanthrene	4.5 ± 0.3	7.3 ± 0.6	5	8.6	10.7
Fluoranthene	7.1 ± 0.5	6.5 ± 0.7	6	11.2	11.8
Pyrene	6.3 ± 0.4	5.6 ± 1.0	6	17.8	18.8
Benz(a)anthracene	2.6 ± 0.3	2.8 ± 0.1	6	4.1	4.1
Chrysene	3.5 ± 0.1	3.4 ± 0.1	6	3.7	3.7
Benzo(b)fluoranthene	6.2 ± 0.3	5.7 ± 0.3 [d]	6	5.0	5.3
Benzo(k)fluoranthene	2.0 ± 0.1	2.2 ± 0.1	6	4.3	4.5
Benzo(a)pyrene	2.9 ± 0.5	2.8 ± 0.2	6	7.8	8.2
Benzo(ghi)perylene	4.5 ± 1.1	3.4 ± 0.2	6	4.9	5.3
Indeno(cd)pyrene	3.3 ± 0.5	4.0 ± 0.1	6	3.4	3.7

a. Mean value $\pm$ s; s = standard deviation.

b. CV = coefficient of variation = 100 • s / mean.

c. Relative precision =100 • CI / mean; CI =95 % confidence interval = t(0.05) • s / $\sqrt{n}$ and t(0.05) = is the value of Student's t at the 95% probability level.

d. Corrected for co-elution of perylene.

Table 4. Reproducibility of determination of particulate PAH in simulated ETS. [a]

PAH	Mean ng m^{-3}	s[b] ng m^{-3}	Mean µg g^{-1}	s µg g^{-1}	Prec[c] %
Phenanthrene	32.0	3.3	16.4	1.7	26.0
Anthracene	1.3	0.2	0.7	0.1	34.0
Fluoranthene	10.8	0.1	5.5	0.1	2.1
Pyrene	8.1	0.8	4.1	0.4	23.4
Benz(a)anthracene	13.0	0.8	6.6	0.4	15.2
Chrysene	32.4	1.1	16.6	0.6	8.3
Benzo(b)fluoranthene	6.6	1.1	3.4	0.6	41.5
Benzo(k)fluoranthene	2.3	0.2	1.2	0.1	17.8
Benzo(a)pyrene	9.1	0.5	4.7	0.3	13.6

a. Four ETS-laden filters were quartered, and four identical composites were assembled and analyzed. One sample was lost. Net ETS particle mass of each composite was 5 mg.

b. s = Standard deviation.

c. Relative precision =100 • CI / mean; CI = 95 % confidence interval = t(0.05) • $s / \sqrt{n}$, n is the number of samples and t(0.05) is the value of Student's t at the 95 % probability level.

Table 5. Reproducibility of determination of gas- phase PAH in ETS in an environmental chamber with co-located IOVPS samplers

PAH	Mean $ng\ m^{-3}$	Difference $ng\ m^{-3}$	CV [a] %
Naphthalene	822	115	12
1- Methylnaphthalene	334	26	7
2- Methylnaphthalene	526	56	9
Biphenyl	45	14	27
Acenaphthene and acenaphthylene	72	17	21
Fluorene	56.5	5.0	8
Phenanthrene	43.1	13.0	15
Anthracene	3.85	0.76	17
Fluoranthene	3.73	0.75	18
Pyrene	13.8	6.0	39
Benz(a)anthracene	0.15	0.04	24
Chrysene	0.86	0.10	10

a. Co-efficient of variation = 100 • standard deviation / mean. Standard deviation was estimated from the difference following ref. 19.

Table 6. Gas-phase emission factors for simulated ETS from Kentucky Reference cigarettes 1R4F. Uncertainties are given as 95% confidence intervals.[a]

	E^b ± $E_{Unc}{}^c$ ng cig^{-1}		F^d ± $F_{Unc}{}^e$ ng $(mg_{ETS})^{-1}$	
Naphthalene	11200	920	858	72
1-Methylnaphthalene	4570	400	349	31
2-Methylnaphthalene	7200	630	549	49
Fluorene	773	167	59.0	12.8
Phenanthrene	590	60	45.0	4.6
Anthracene	52.7	4.9	4.02	0.38
Fluoranthene	51.0	4.8	3.89	0.37
Pyrene	189	40	14.4	3.0
Benz(a)anthracene	2.1	0.3	0.157	0.022
Chrysene	11.8	1.7	0.898	0.132

a. From concentration measurements for one hour in a sealed $36m^3$ chamber, starting 30 min. after 3 cigarettes were smoked. Average of measurements from two co-located IOVPS.

b. E=emission factor in units of mass per cigarette. $E = Cva(dt) / n(e^{-at_i} - e^{-at_f})$, where C = concentration in ng m^{-3}, v=chamber volume, a=total air exchange rate, (including air removed by sampling), dt=net sampling time, t_i=initial sampling time in minutes after smoking, t_f=time at the end of sampling, and n=number of cigarettes.

c. E_{Unc}=uncertainty in emission factor calculation; $(dE/E)^2 = (dC/C)^2 + (da/a)^2 + (d(e^{-at_i} - e^{-at_f}) / (e^{-at_i} - e^{-at_f}))^2$. The uncertainty in measurement of concentration is given by $(dC/C)^2=(dP/P)^2+(dO/O)^2+(dR/R)^2$ $(dV/V)^2$. The terms represent fractional uncertainties in measurement of peak heights P (assessed from repetitive injections), peak heights when nearby peaks overlap O, recovery of internal standards R, and sample final volume V, respectively. Other factors contributed insignificantly to the measurement uncertainty.

d. F=emission factor per mg particulate ETS = E/M, where M=0.958 mg m^{-3}, the total suspended particulate mass concentration..

e. F_{Unc}=uncertainty in F, where $(dF/F^2)=(dC/C)^2+(dM/M)^2$.

Table 7. Particle-phase emission factors for simulated ETS from Kentucky Reference cigarettes 1R4F. Uncertainties are given as 95% confidence intervals.[a]

	E^b ± $E_{Unc}{}^c$ ng cig^{-1}		Literature E^d ± $E_{std\ dev}{}^e$ ng cig^{-1}		F^f ± $F_{Unc}{}^g$ ng $(mg_{ETS})^{-1}$	
Phenanthrene	<71	nd			<5.4	nd
Anthracene	<1	nd			<0.1	nd
Fluoranthene	31	1			2.4	0.1
Pyrene	41	10			3.1	0.7
Triphenylene	85	20			6.5	1.5
1,2-Benzofluorene	36	8			2.7	0.6
Benz(a)anthracene	152	23			11.6	1.8
Chrysene	412	36			31.4	2.8
Benzo(b)fluoranthene	132	55	112	15	10.0	4.2
Benzo(k)fluoranthene	32	6	34	5	2.5	0.4
Benzo(a)pyrene	74	10	113	15	5.7	0.8

a. Concentrations were measured for one hour in a sealed 36 m^3 chamber, starting 30 min. after 3 cigarettes were smoked. Average of measurements from two co-located IOVPS.

b. E=emission factor in units of mass per cigarette. $E = Cva(dt)/n(e^{-at_i} - e^{-at_f})$, where v=chamber volume, a=total air exchange rate, (including air removed by sampling), dt=net sampling time, t_i=initial sampling time in minutes after smoking, t_i=time at the end of sampling. n=number of cigarettes.

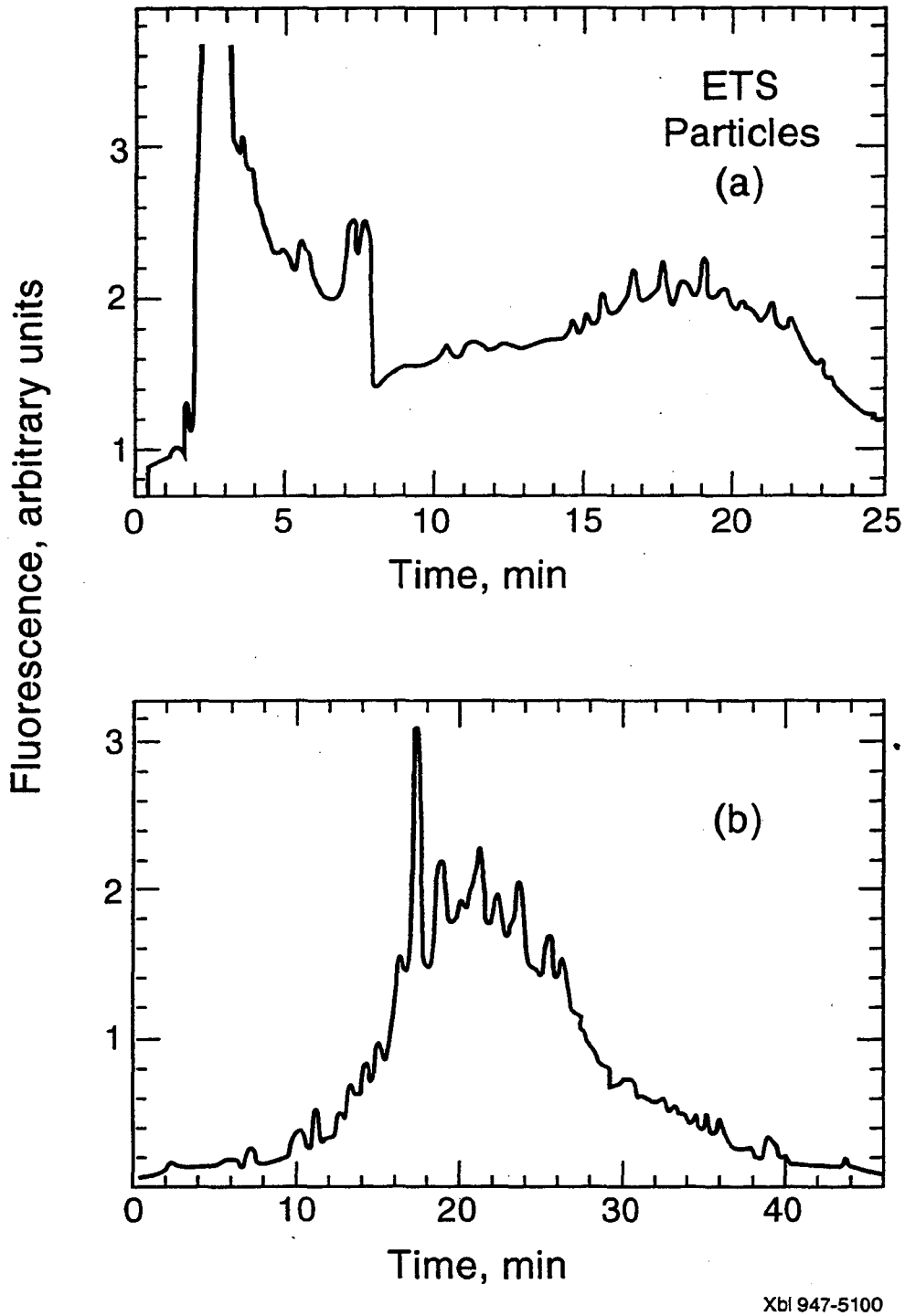
c. E_{Unc}=uncertainty in emission factor calculation; $(dE/E)^2 = (dC/C)^2 + (da/a)^2 + (d(e^{-at_i} - e^{-at_f})/(e^{-at_i} - e^{-at_f}))^2$. The terms are defined in footnote c of Table 6. The relative precision data of Table 4 were used for dC/C. The values of dC/C for triphenylene and 1,2-benzofluorene were estimated from the relative precisions for pyrene.

d. Literature values from ref. 6.

e. Uncertainties given as standard deviations.

f. F=emission factor per mg particulate ETS = E/M, where M=0.958 mg m^{-3}, the mass concentration of total suspended particulate matter.

g. F_{Unc}=uncertainty in F, where $(dF/F)^2=(dC/C)^2+(dM/M)^2$.



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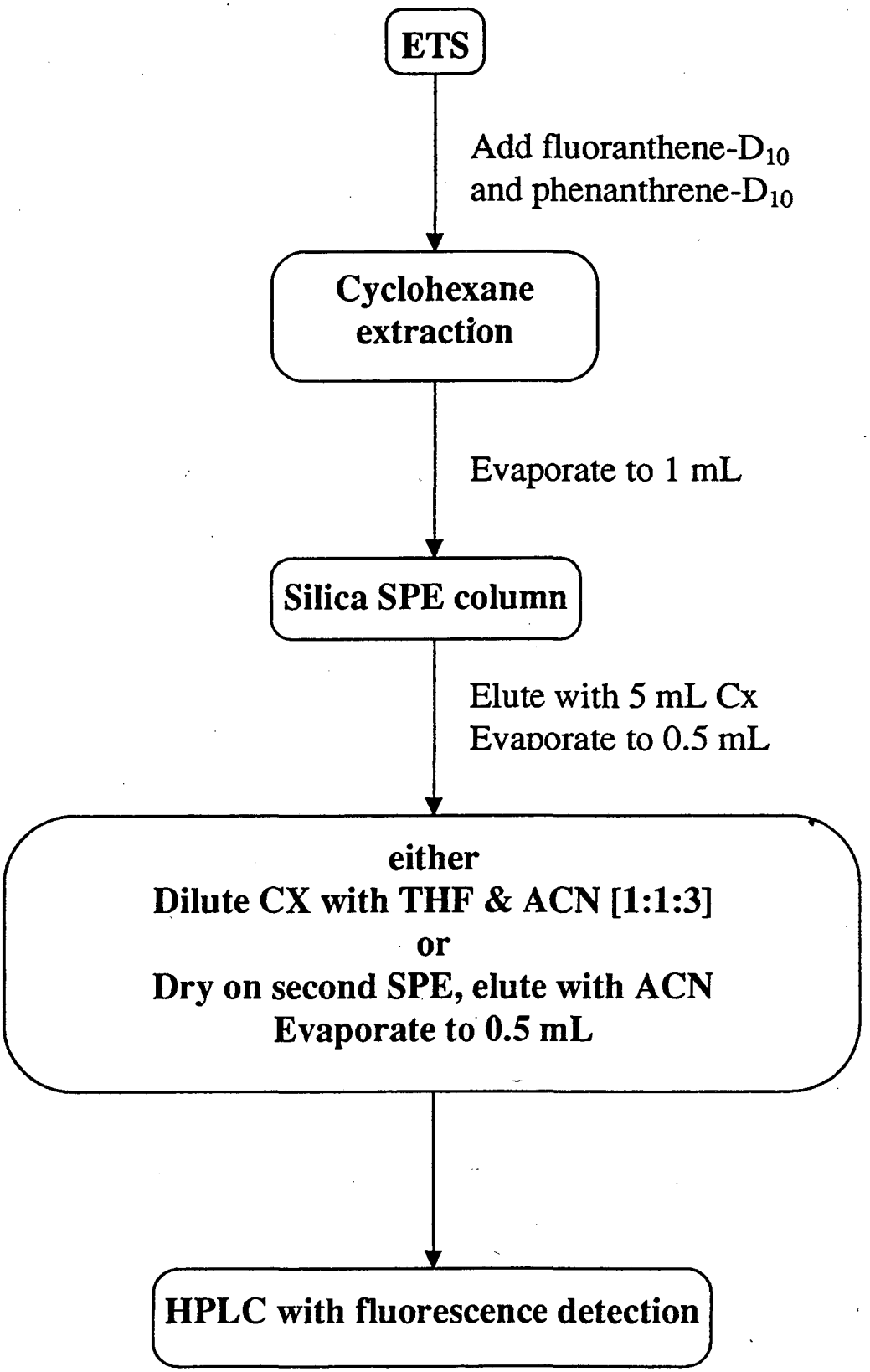

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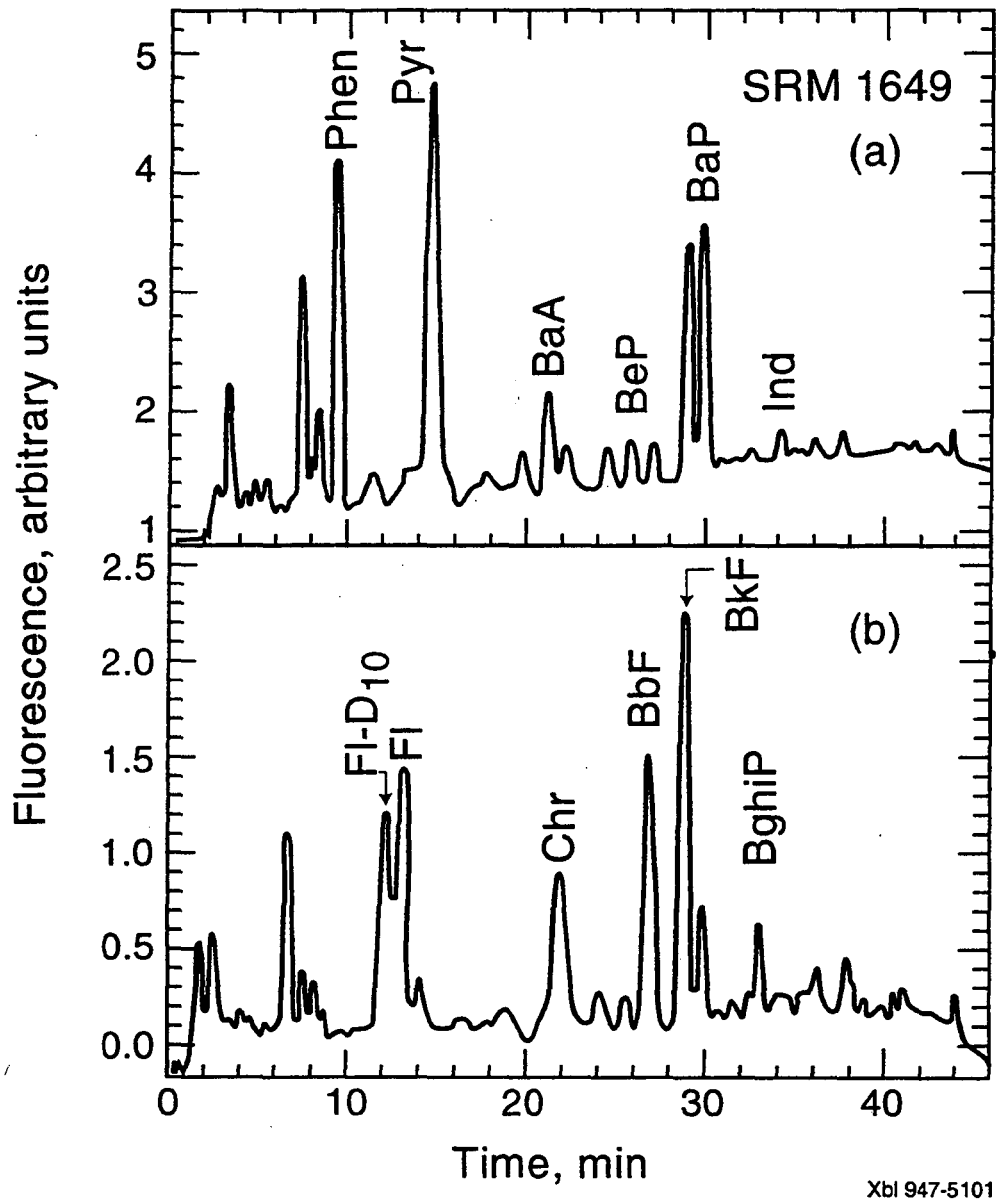

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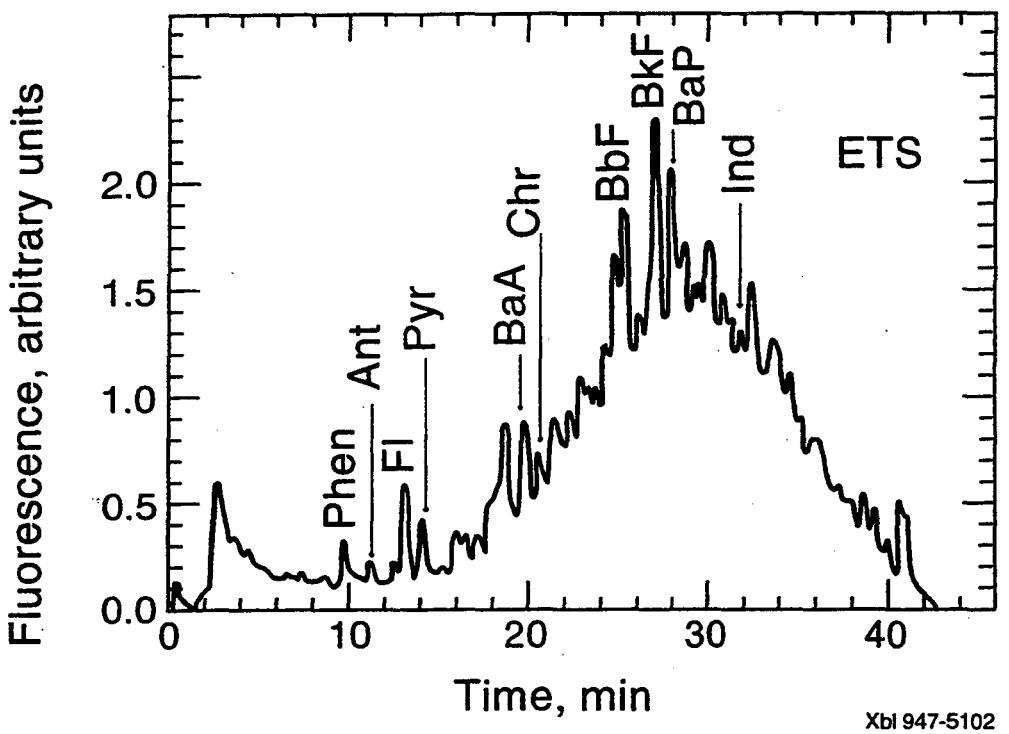

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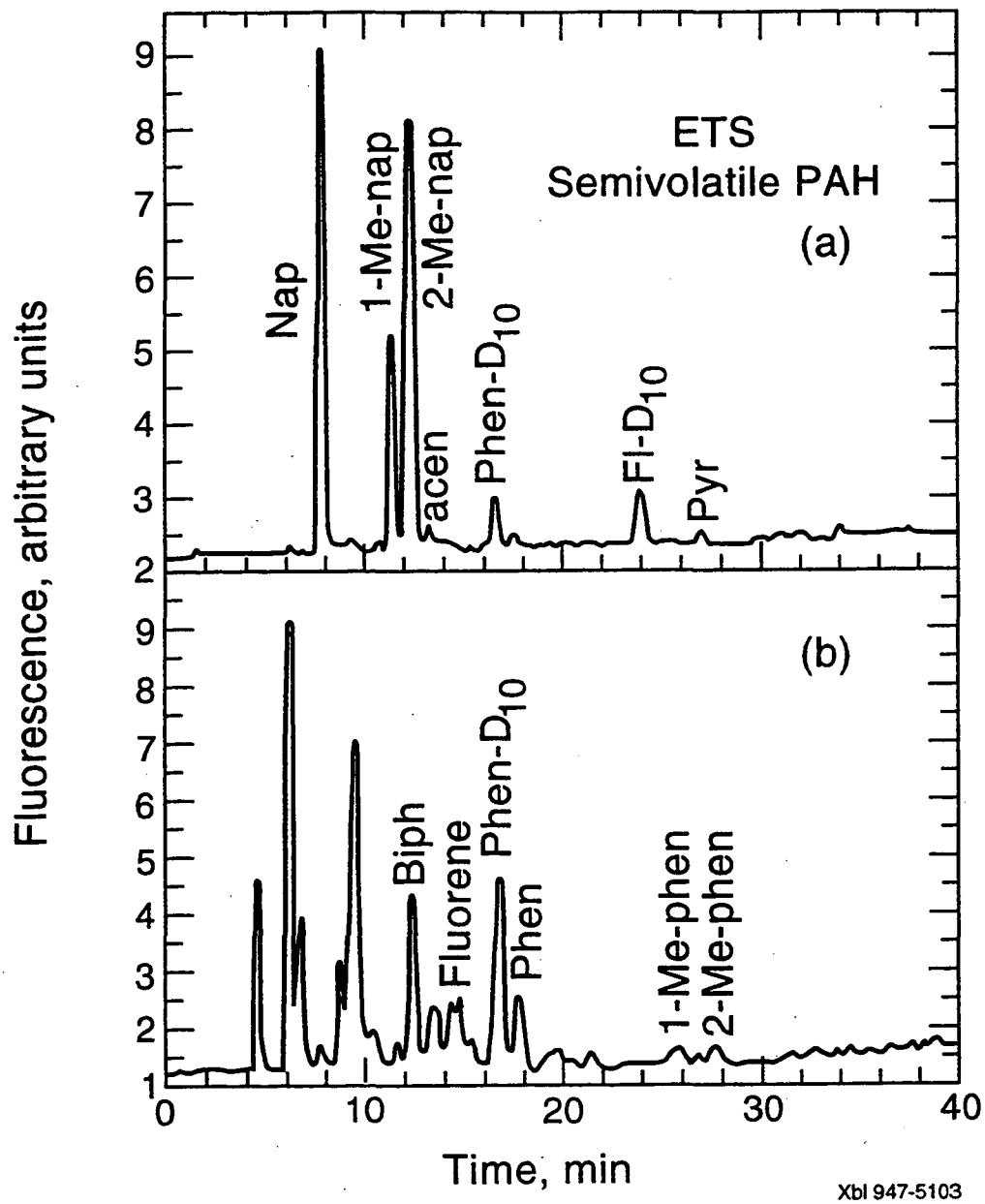

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