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REAL-TIME MONITORING OF POLYCYCLIC AROMATIC HYDROCARBONS AND RESPIRABLE SUSPENDED PARTICLES FROM ENVIRONMENTAL TOBACCO SMOKE IN A HOME

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ABSTRACT

Real-time measurement of polycyclic aromatic hydrocarbons (PAH) on fine particles was evaluated in a home with environmental tobacco smoke (ETS) as a source. The PAS 1000i PAH monitor (EcoChem Technologies, Inc., West Hills, CA) is based on photoelectric ionization of surface PAH, loss of the photoelectrons, and subsequent measurement of the remaining positively charged particles in a filter electrometer. Cigarettes were smoked in the living room of a small house, with the time series of PAH concentrations logged with high time resolution using a Langan DataBear L15 data logger. Respirable suspended particles (RSP) were monitored using the Model 8510 Piezobalance (TSI, Inc., St. Paul, Mn), which measures fine particle concentrations with 2-min averaging periods. Comparison of PAH and RSP concentrations from these experiments suggests: (1) the PAH concentrations for the two types of cigarettes -- a regular Marlboro filter cigarette and a University of Kentucky reference cigarette No. 2R1 -- were similar, but the RSP concentrations were different; (2) concentrations from the real-time PAH monitor were linearly related to RSP concentrations; (3) the slopes of the regression lines between PAH and RSP differed for the two types of cigarettes. The real-time PAH monitor appears to be useful tool for evaluating mathematical models to predict the concentration time series in indoor microenvironments.

INTRODUCTION

Measurement approaches that rely on collection devices (for example, pumps and filters) often give averages as long as 12 hours or more. Development of mathematical models of human exposure to pollutants in indoor settings requires monitoring instruments that have rapid time responses (usually less than two minutes), or "real-time" instruments. Real-time measurements are needed because human activities (for example, smoking a cigarette, burning toast, using a chemical spray) often occur for a few minutes or less. For example, indoor air quality models such as the Sequential Cigarette Exposure Model (SCEM; Ott, Langan, and Switzer, 1992) compute the time series of indoor pollutant concentrations for smoking activities with a time resolution of 10 seconds. Although real-time measurement methods do not exist for many pollutants, a real-time monitoring instrument has been introduced for polycyclic aromatic hydrocarbons, the PAS 1000i PAH monitor (EcoChem Technologies, Inc., West Hills, California). This paper explores the application of this new monitor to a practical problem: measuring the concentrations time series generated by ETS in a home.

Polycyclic Aromatic Hydrocarbon (PAH) Monitor

The PAS 1000i PAH monitor operates using the principle of photoelectric ionization of surface PAH, loss of the photoelectrons, and subsequent measurement of the remaining positively charged particles in a filter electrometer. Burtscher and Schmidt-Ott (1984) presented the first results on the response of a photoelectric aerosol sensor (PAS) showing qualitatively that, with the combination of a relatively large irradiation unit and a sensitive electrometer, an instantaneous detection of PAH is possible. Niessner (1986) examined the response characteristics of the sensor to different PAH to determine if there is a preference in charge due to the molecular structure of the PAH. Observing the normalized concentration of charged particles at different particle sizes, he found a quantitative linear relationship between the surface area and the photoelectric activity. The correlation coefficient between the PAH amount (at the surface) and photoelectric activity was above $r = 0.998$ ($n = 8$ measurements) , indicating that the sensor signal reflects the amount of PAH present. He concluded that the PAS methodology allowed for continuous, sensitive (under ng/m^3) *in situ*-monitoring of four-and-higher-ring PAH. As long as the PAH are enriched in sub-monolayers, which is usually the case in combustion situations, the method yielded quantitative information on the amount of adsorbed PAH. Niessner and Walendzik (1989) examined the response of the PAS monitor to cigarette smoke. They found that the PAS results correlated well ($r = 0.94$, $n = 20$) with benzo[a]pyrene (BaP) concentration, which was determined independently by *in situ* synchronous fluorimetry on TLC plates. The absolute lower detection limit was about 50 pg.

Wilson *et al.* (in press) compared readings from the commercially available PAS 1000i monitor (EcoChem Technologies, Inc., West Hills, California) with 12 integrated measurements of PAH collected by a pump-driven sampler in homes and offices with smokers. The collection device included an annular denuder to remove vapor-phase PAH, a 2.5 μm impactor to remove coarse particles, and an XAD-2 resin cartridge to collect any PAH vaporized from the particles on the filter during sampling. The integrated monitors operated over an 8-h period with a sampling volume of 20 L/min, and the filter and resin were extracted with dichloromethane, with the extract analyzed by gas chromatography/mass spectrometry (GC/MS). Comparison of the PAS 1000i with the integrated samples showed that the results were highly correlated ($R^2 = 0.985$). They found the instrument easy to operate, rugged for use in field settings, stable, and reliable. It had a low limit of detection (around 10 ng/m^3) and was highly sensitive to variations in concentrations in indoor settings. They recommended replacement of the electrostatic precipitator (ESP) with a straight stainless steel tube, since the ESP is not needed for indoor and ambient aerosols. The PAS 1000i used in the present study was modified in this manner, and a newer model, the PAS 1002i, is now available from the manufacturer.

Respirable Suspended Particle (RSP) Monitor

The piezobalance originally was developed to monitor RSP levels in occupied buildings in Japan, because Japanese law requires measurement of RSP levels several times each day in stores, offices, apartments, and other buildings. The theory, performance characteristics, size selectivity, and history of its design are found in papers by Olin, Sem, and Christenson (1970), Olin and Sem (1971), Carpenter and Brenchley (1972), Daley (1974), Daley and Lundgren (1975). Sem, Tsurubayashi, and Homma (1977) found, over the range of 50-5,500 $\mu g/m^3$, that readings from 11 piezobalances were generally within $\pm 10\%$ and always within $\pm 15\%$. The TSI Model 8510 piezobalance is a portable instrument designed for measuring the mass concentration of fine particles with a 3.5 μm cutpoint.

METHODOLOGY

Real-time concentration readings from the PAS 1000i PAH monitor with the ESP removed were compared with successive 2-minute average concentrations from two Model 8510 piezobalances in the living room of a home. Two different types of cigarettes were smoked: a regular Marlboro filter cigarette (Experiment A) and a University of Kentucky research cigarette reference No. 2R1 (Experiment B). The instruments were collocated on a stand 0.5 m above the floor of the living room but were not connected to a common intake port; the intake ports were within 0.5 m of each other. In each experiment, two cigarettes of the same type were smoked sequentially one after another. The time series of concentrations from the two piezobalances were recorded manually every 2 minutes from the instrument's digital display, while the concentrations from the PAH monitor were recorded electronically at 10-second intervals using a Langan L15 DataBear data logger (Langan Products, Inc., San Francisco, California). The DataBear data logger was attached to a Macintosh IIsi personal computer that displays the concentrations on its color monitor in real time. At the end of the experiments, the data generated by the PAH monitor were downloaded into the Macintosh computer.

The home -- a single-story, two-bedroom, one-bathroom structure -- was 606 ft^2 (56.3 m^2) with a volume of 139 m^3. The area of the living room was 151 ft^2 (4.28 m^2), and its volume was 35.7 m^3. During the experiments, the adjoining door to the kitchen was open 2"; the adjoining door to the bedroom was open 2"; and the front door of the home, which opens into the living room, was closed. One window in the living room was closed and the other was opened 6" to give a higher than usual ventilation rate for wintertime to enable the experiments to be completed within a reasonable time.

RESULTS

Comparing the two piezobalances with each other for the Marlboro cigarette in Experiment A (Figure 1, top) shows that the resulting regression line has a slope of nearly unity (RSP2/RSP1 slope = 1.12) with $R^2 = 0.86$ ($n = 49$), indicating that readings from the two piezobalances are correlated with each other and have little bias. A similar regression of the PAH readings versus one piezobalance (Figure 1, bottom) shows a high correlation ($R^2 = 0.88$, $n = 50$), but the PAH/RSP slope = 0.0138. This result indicates that the PAH readings are correlated with the RSP readings and that the PAH concentrations for the Marlboro filter cigarette are about 1.38% of the RSP concentrations.

For the Kentucky 2R1 cigarette (Figure 2, top), Experiment B also shows good agreement between the two piezobalances (RSP2/RSP1 = 1.11) and a high correlation ($R^2 = 0.88$; $n = 38$). Two outlier data points above 700 $\mu g/m^3$ have been excluded from the regression, because random outliers often occur during the "source-on" period in chamber experiments (Furtaw, 1994). Occasional deviations between the two piezobalances are not surprising for two-minute averages, since the instruments are next to each other but are not connected to a common sampling intake. The regression analysis of the PAH readings versus both piezobalances (Figure 2, bottom) shows a moderate correlation ($R^2 = 0.66$; $n = 32$), and the PAH/RSP slope = 0.006. Thus, for the Kentucky 2R1 research cigarettes, the PAH readings are moderately correlated with the RSP readings, and the observed PAH concentrations are about 0.6% of the RSP concentrations.

The much lower value of the PAH/RSP ratio for the Kentucky 2R1 research cigarettes than for the Marlboro cigarettes is consistent with the relative slopes of the regression lines, which have a ratio of 0.0138/0.006 = 2.3. Comparison of the source strengths from the two types of cigarettes indicated that both types emitted about the same amount of PAH, but that the RSP emission was about 2.3 times higher for the research cigarette than for the Marlboro filter cigarette.

CONCLUSIONS

This study indicates that a real-time PAH monitor using a photoelectric aerosol sensor (PAS) can generate concentration time series that are useful for measuring effective air exchange rates and evaluating indoor air quality models. In experiments with cigarette smoke as a source, the PAH monitor showed a high correlation with RSP concentrations measured using a piezobalance. The similarity in PAH levels measured by the PAS but the difference in RSP concentrations for two types of cigarettes (a Marlboro filter versus a Kentucky Research 2R1) indicate that the PAH monitor is measuring a particular subspecies of the particles, as it should be, and is not just responding to changes in the mass concentration. The broad sensitivity range of the PAH monitor spanned three orders of magnitude, and its ruggedness and reliability suggest it is well suited for exposure model development and validation experiments in homes and other locations. Because the instrument is relatively small and can be adapted for battery operation, it can also be used in motor vehicle exposure field studies.

DISCLAIMER AND ACKNOWLEDGEMENT

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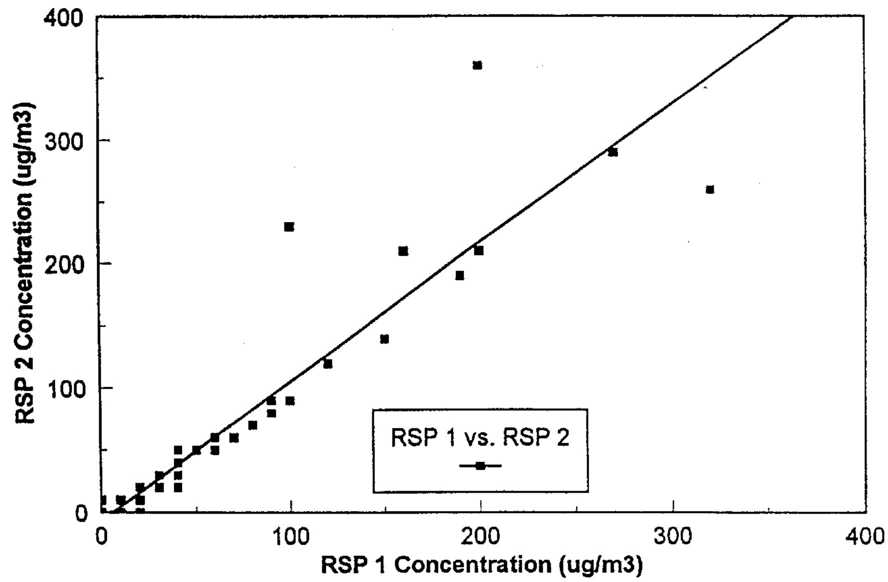


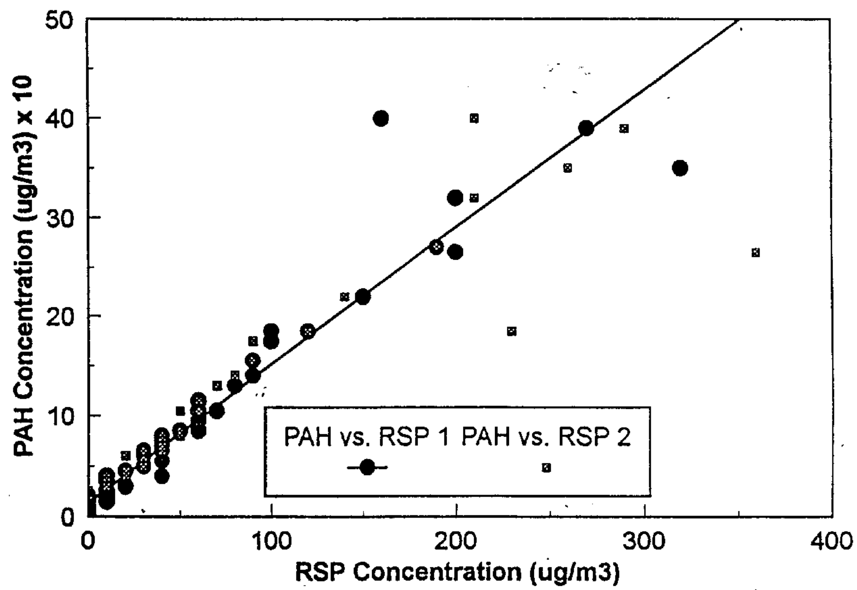
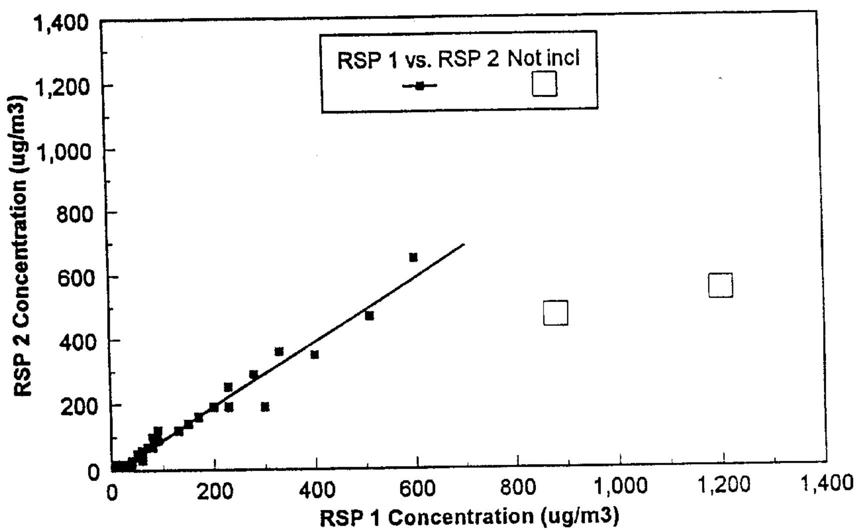


Figure 1. Comparison of two piezobalances (RSP 1 and RSP 2) and comparison of PAH and one piezobalance for the Marlboro filter cigarettes (Experiment A).



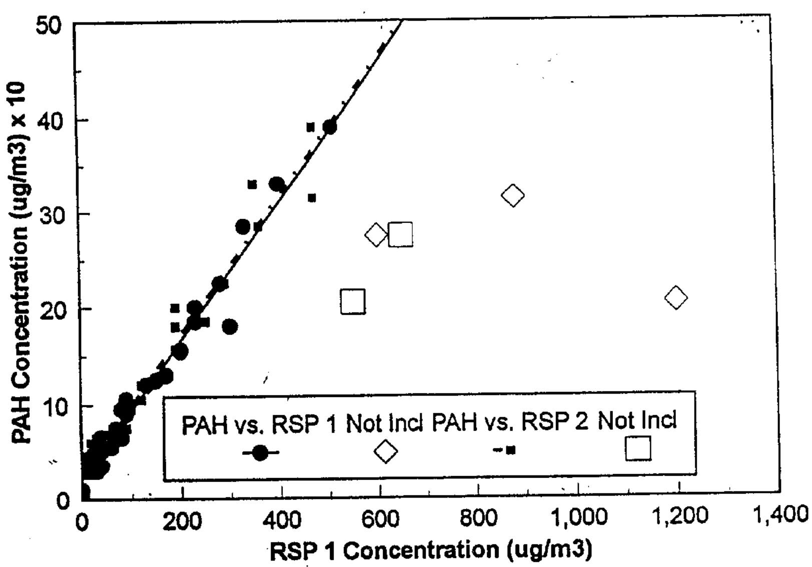


Figure 2. Comparison of two piezobalances (RSP 1 and RSP 2) and comparison of PAH and one piezobalance for the Kentucky Research 2R1 cigarettes (Experiment B).