



Project Summary

Evaluation of a Gossen, GmbH Model PAS 1001i Photoelectric Aerosol Sensor for Real-Time PAH Monitoring

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The objective of this study was to evaluate the performance of a Model PAS 1000i Photoelectric Aerosol Sensor (also referred to in this report as the "PAH Analyzer" for real-time monitoring of polycyclic aromatic hydrocarbons (PAH) in air. Three tasks were conducted in the study: 1) vapor tests, 2) particle tests, and 3) integrated sampler comparison tests. In the vapor tests, benzene and PAH vapors were introduced individually into a 17 m³ environmental chamber as vapors, with the chamber air concentrations monitored by a Trace Atmospheric Gas Analyzer (TAGA). The concentrations of the spiked chemicals in the air ranged from 200 ppb for 1-methylnaphthalene to 500 ppb for benzene. The PAH analyzer did not yield any response when sampling these chemical vapors.

In the particle tests, sodium chloride aerosols of various sub-micron sizes (0.05-0.5 μm in diameter) were generated and then sampled by the PAH analyzer to determine whether the instrument responded only to aerosols containing PAH. The results showed that the PAS did respond to NaCl aerosol that was anticipated to contain no PAH. This response depended on the size and number concentration, and was a small fraction of the typical response obtained at particle sizes and concentration levels common in indoor air (for example, 0.1-0.3 μm diameter, 10,000-50,000 particles/cm³). Further step-by-step tests confirmed that the analyzer's response did result from the passage of the aerosol through the ultraviolet radiation cell. The origin of this response could not be resolved in this

study, but possible causes of the response to non-PAH aerosol were explored.

In the integrated sampler comparison study, two Battelle-developed indoor PAH samplers were collocated with the PAH analyzer in indoor environments with and without the presence of environmental tobacco smoke (ETS). The fine particle-bound (<2.5 μm) PAH concentration in the air sampled was then estimated by summing the fine particle concentrations of individual PAH and alkylated PAH species determined by gas chromatography-mass spectrometric (GC/MS) analysis of the filters and XAD-2 sorbent traps from the integrated samplers. The response of the PAH analyzer (in pAmp) over the corresponding sampling periods was also averaged and then converted to a PAH concentration using the manufacturer's suggested conversion factor of 3000 ng/m³/pAmp.

In the presence of ETS, the PAH analyzer concentrations were approximately 4 times higher than the fine particle PAH concentrations derived from the integrated samplers. In the absence of ETS, the PAH analyzer concentration was similar to the fine particle-bound PAH concentration in one test, but was only one-third of the fine particle PAH in the other test. It was also observed from the tests conducted that the PAH analyzer yielded a larger unit response to PAH in the ETS aerosol than to PAH in the non-ETS indoor aerosol.

This Project Summary was developed by EPA's National Exposure Research Laboratory, Research Triangle Park, NC,



to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The PAH analyzer evaluated in this study was a Model PAS 1000i Photoelectric Aerosol Sensor manufactured by Gossen, GmbH (Erlangen, Germany) and obtained in the U.S. with ancillary data acquisition software from EcoChem Technologies, Inc. (West Hills, CA).

The PAH analyzer is based on the principle of photoelectric aerosol charging reported in the literature within the last decade. The presence of a mono- or submono-layer of PAH compounds adsorbed on the surface of aerosol particles allows UV-light induced photoemission of electrons from electron-rich PAH molecules that are adsorbed onto a mono-layer on the surface of a particle. This phenomenon, also referred to as aerosol photoemission (APE), is the measurement principle used in the PAH analyzer evaluated in this study.

The aerosol sampled enters the analyzer via an electrofilter. The electrofilter in the PAS 1000i has a nominal operating voltage potential of ≈ 465 V, and removes all the ions and a fraction of the charged particles that may be present in the air being sampled. The aerosol exiting the electrofilter enters the UV irradiation cell where it is irradiated and APE occurs. In principle, APE results from the PAH-adsorbed aerosols at particle sizes $< 1 \mu\text{m}$. The net APE signal is minimal at particle sizes $> 1 \mu\text{m}$ in diameter; at these sizes recapture of the photo-emitted electrons by the particles is believed to occur too rapidly to permit the charged particles to be detected. The photoemission of electrons by PAH adsorbed on the surfaces of aerosol particles causes the particles themselves to become positively charged. The charged aerosol is then brought through an electrically isolated conduit to an electrometer. The current measured by the electrometer is then a sensitive indicator of the degree of APE occurring in the UV irradiation cell.

Previous evaluation studies reported in the literature have reported that APE arises only from PAH adsorbed on aerosols. At the UV irradiation energy used of ~ 4.2 eV no other adsorbate was found in these studies to result in an APE signal in these laboratory APE systems. In addition, the APE signal was found to be proportional to the amount of adsorbed PAH, up to the limit of a monolayer on the surface of a

particle. Researchers have suggested, however, that in typical residential combustion exhausts and except for residential wood combustion, the particle number concentrations emitted are sufficiently high in relation to the PAH mass emitted that only low PAH surface coverages are likely to result. Under these circumstances, the net APE response could continue to be proportional to the total adsorbed PAH.

In addition to these characteristics, the APE signal from the analyzer varies with the PAH compound adsorbed on the particle surface, with the highest response associated with large π -electron systems. Of the PAH compounds tested, coronene was the most photoelectrically active. The nature of the surface on which the PAH compounds are adsorbed also affects the APE response. For each type of particle surface, however, the response generally increases linearly with increasing surface-adsorbed PAH mass.

Various studies with laboratory APE systems have shown that for specific sources of PAH aerosols, such as cigarette smoke, oil stoves, spark-ignition engines, etc., the APE signal is reasonably correlated with the concentration of particle-phase PAH compounds measured by wet-chemical techniques. This result is consistent with the two characteristic response features described above, since the mix of PAH compounds and the aerosol surface characteristics would tend to remain generally constant for a specific source of particulate-phase PAH.

The APE signal can be expected to be less correlated with the particle-phase PAH concentration when the mix of PAH compounds and the aerosol surface characteristics in the air sampled are more variable. This situation is of significant interest in evaluating the PAH analyzer as a reliable indoor screening or monitoring tool since indoor air can conceivably contain particulate-phase PAH originating in varying proportions from many different aerosol sources such as ETS, woodstoves, burners, fireplaces, combustion-derived aerosols in outdoor air, etc. An evaluation of the relationship between the PAH analyzer's response and measured PAH in different indoor environments has, however, not been previously conducted.

The objective of this study was to evaluate the overall performance of the PAH analyzer in monitoring PAH indoors, with the following three tasks:

- (1) Vapor tests to verify that the PAH analyzer does not respond to PAH vapors, as reported previously in the literature.

- (2) Particle tests to determine the response of the PAH analyzer to sodium chloride (NaCl) test aerosols and to determine whether the PAH analyzer has the desired selective response for only PAH containing aerosols.
- (3) Integrated sampler comparison tests to compare the indoor PAH concentrations determined from conventional integrated sampling and subsequent GC/MS analyses with the average responses over corresponding sampling periods from the collocated PAH analyzer.

Procedure

A brief description of the procedures used to conduct the three tasks is provided here:

- (1) Benzene and PAH vapor tests: Tests of the PAH analyzer's response to benzene, p-dichlorobenzene, naphthalene, 1-methylnaphthalene, quinoline, 1-chloronaphthalene, and indene were conducted by introducing the vapors individually into a 17 m^3 environmental chamber and monitoring the chamber air concentrations by a Trace Atmospheric Gas Analyzer (TAGA). The concentrations of the spiked chemicals in the chamber air ranged from 200 ppb for 1-methylnaphthalene to 500 ppb for benzene. An aliquot of each of the chemicals was injected through a heated injection port where it was vaporized, and subsequently dispersed into the chamber. Prior to injection, the chamber was flushed with AADCO zero air. During the experiment, the chamber was sampled by the TAGA, the PAH analyzer, and by a TSI Model 3020 condensation nucleus counter (CNC) for monitoring the particle concentration in the chamber. The measured concentration of the spiked vapor was recorded for each test, together with the humidity, temperature, and particle concentration in the chamber atmosphere, and the response of the PAH analyzer when sampling from the chamber.
- (2) Particle tests: NaCl test aerosols in the 0.05 - $0.5 \mu\text{m}$ size range were generated using a nebulizer that generates a droplet spray by aspirating a solution of NaCl from a reservoir (analytical grade NaCl, muffled at 400°C for 4 hours was used to prepare the salt solution).

The nebulized droplets were dried either by heating in a coiled copper tube maintained at $\sim 150^{\circ}\text{C}$ or by dilution with dry air. The solid salt particles were then brought to a state of charge equilibrium by passage through a radioactive Kr-85 neutralizer (2 mCi, 5/89). The neutralized aerosol was mixed with dry, filtered air and introduced into a Plexiglas aerosol mixing chamber from which it was sampled by the PAH analyzer and two aerosol measurement instruments, a TSI, Inc. Model 3020 CNC and a PMS, Inc. Model LAS-X Laser Aerosol Spectrometer. Size distributions of the test aerosols were measured by coupling a TSI Model 3040/3042 Diffusion Battery with the CNC.

Apart from the NaCl aerosol tests, deionized water without dissolved salt was nebulized, dried, and sampled from the aerosol chamber to establish background conditions. Carrier air alone was also sampled from the aerosol chamber in other background tests. A second series of detailed PAH analyzer tests were also conducted in which two specific components of the analyzer, namely the electrofilter and the UV lamp were turned off selectively without disabling the electrometer. These detailed tests of the response of the PAH analyzer to NaCl test aerosols were conducted using a 660-1 stainless steel chamber. The large chamber allowed the test aerosols to be aged for several hours to simulate a typical indoor aerosol before being sampled by the PAH analyzer.

- (3) Integrated sampler comparison tests: The integrated sampler system consisted of two sampling trains. The first used a Battelle-developed indoor sampler equipped with an open-face 47-mm quartz fiber filter upstream of an XAD-2 resin trap and collected the combined vapor and particle-phase PAH. The second train consisted of the following components (listed in the order of air flow), impactor-denuder-quartz fiber filter-XAD trap, and was designed to collect fine particle-bound ($<2.5\ \mu\text{m}$) PAH in the sampled air stream. The sampling flow rate through the two sampling trains was controlled at $20.0 \pm 0.2\ \text{lpm}$ using a pump and a metering valve and was monitored

continuously by an in-line mass flow meter.

The filter and XAD-2 trap from each integrated sampler were combined and extracted with dichloromethane (DCM) by the Soxhlet technique. The DCM extract was concentrated by Kuderna-Danish (K-D) evaporation. The extract was then analyzed by electron impact (EI) GC/MS for target PAH and alkylated PAH species.

Four sets of indoor integrated samples were collected during the study: two tests were performed in the presence of ETS and two tests were conducted without ETS. The sampling periods employed in the tests varied between 8 and 24 hours depending on the presence or absence of ETS. During each test, the PAH analyzer was collocated with the two sampling trains and the response over the sampling period was continuously recorded and stored in a data acquisition computer. During all tests, a TSI Model 3020 CNC was used to monitor the particle concentrations in the indoor environment being sampled. The particle number concentration measured by the CNC was recorded by a strip-chart recorder that also recorded the PAH analyzer response during the sampling intervals.

Results

Benzene and PAH Vapor Tests. The PAH analyzer did *not* yield a response when sampling chamber air containing each of the various chemical vapors. This finding agrees with the published literature reports that the PAH analyzer does not respond to vapor-phase PAH compounds. The series of seven chamber tests were conducted at low humidity conditions (9% relative humidity at $23\text{--}25^{\circ}\text{C}$), and particle concentrations in the chamber remained below $1\text{--}2\ \text{particles}/\text{cm}^3$ in all tests, i.e., there was minimal possibility for water vapor-induced hydrolysis and/or condensation processes that might result in particles with surface-adsorbed PAH. Additional vapor tests were conducted subsequently at chamber humidity conditions of $\sim 80\%$, using similar vapor concentrations and temperature conditions. These tests also showed no PAH analyzer response to vapor-phase PAH in all except one case. In the one case where a response was observed, for indene, a substantial particle concentration of $\sim 50,000\ \text{particles}/\text{cm}^3$ was measured in the cham-

ber suggesting that the observed PAH analyzer response was due to the adsorption of vapor-phase PAH onto particle surfaces. The particle formation observed was traced to the polymerization of the aged indene liquid used in the test (Merck Index). A more detailed discussion of these tests will be reported separately.

Particle Tests. The PAH analyzer did not show any response during the background tests, when sampling either dry, filtered air or filtered air carrying dried, deionized water droplets from the nebulizer. The PAH analyzer did, however, show a response when sampling the three different NaCl test aerosols generated at various number concentrations in the aerosol chamber (the test aerosols had log-normal size distributions and geometric mean diameters of ~ 0.04 , ~ 0.08 , and $\sim 0.15\ \mu\text{m}$). The non-zero PAH analyzer response increased approximately linearly with particle concentration and with increasing test particle size. More detailed tests conducted subsequently also established that the response observed was definitely a result of the passage of the test aerosol through the UV irradiation cell. The magnitude of the response observed for NaCl particles is generally smaller than that observed in either typical indoor air containing low, background amounts of PAH-coated particles or high concentrations of cigarette smoke particles.

An analysis of the PAH content of the muffled bulk NaCl used in preparing the salt solutions was conducted using DCM extraction and GC/MS analysis. PAH was not detected in the bulk salt extract, but trace amounts of aliphatic hydrocarbons and phthalates were detected. It is possible that the observed signal is related to other unknown organic species, and this possibility could be examined further in a future study.

While the results obtained in this study appear to contradict literature reports by other researchers, recent tests in November 1992 by Burtcher and co-workers in ETH, Zurich (a research group closely involved with the development of the Gossen PAS) using a laboratory APE system also found APE response to nebulized NaCl tests aerosols. These responses were found to be of a similar magnitude as those found in this study. Further, Burtcher et al. found that APE is eliminated by using an evaporation-condensation NaCl aerosol generator that involves heating the bulk NaCl to a temperature of $\sim 700^{\circ}\text{C}$, suggesting that trace organic contamination may indeed be responsible for the observed APE response from nebulized NaCl aerosols.

Integrated Sampler Comparison Tests.

The integrated sampler comparison tests were used to conduct comparisons between the vapor+particle-phase PAH and fine particle-bound PAH concentrations from the integrated samplers and the PAH analyzer's average response (in pAmp) over the corresponding sampling interval. The fine particle-bound ($< 2.5 \mu\text{m}$) PAH concentration was estimated by summing the fine particle concentrations of individual PAH and alkylated PAH species determined from GC/MS analysis. PAH concentrations were calculated from the average PAH analyzer response for each corresponding test using the conversion factor of $3,000 \text{ ng/m}^3/\text{pAmp}$ provided by Gossen, GmbH.

The average PAH concentrations from the PAH analyzer were about 4 times higher than the measured fine particle PAH concentrations for the two tests conducted in the presence of ETS. In the absence of ETS, the average PAH concentration from the PAH analyzer was similar to the measured fine particle PAH concentration from the integrated sampler in one test but was one-third of the fine particle PAH concentration in the other test.

Conversion factors were also derived on the basis of the fine particle PAH concentrations and the PAH analyzer's average response in each of the four tests. The calculated conversion factors were similar for the two tests within the ETS category, when fine particle PAH was defined either as the sum of all species, or the sum of ≥ 3 -ring species. Within the non-ETS category, the calculated conversion factors from one test were significantly higher than the conversion factors calculated from the data collected in the other test. The conversion factors derived from the tests were generally within (with the exception of the one non-ETS test) the range of the various instrument calibration functions provided by Gossen, GmbH.

Another observation that was also evident from the non-ETS and ETS tests is that the instrument response (in pAmp) was considerably higher when sampling cigarette smoke aerosols than it was to the general indoor aerosol. This result is consistent with reports in the literature that APE is the highest (per unit mass) from PAH such as coronene, benzo(g,h,i)perylene, benzo(e)pyrene, and benzo(a)pyrene, all of which are species present in ETS aerosol. Another possible reason for this higher response rate for ETS aerosol is that a greater fraction of the PAH in these freshly generated aerosols may be present in a surface-adsorbed state compared to the typical, aged non-ETS indoor

aerosol. There may also be differences in the surface characteristics of ETS aerosols that result in a higher response rate compared with non-ETS indoor aerosol.

Conclusions and Recommendations

The following conclusions can be drawn from this study:

- (1) The PAH analyzer does not yield a response when sampling air from a test chamber atmosphere spiked with benzene and PAH vapors. In these tests, the aerosol concentration in the chamber remained below $10 \text{ particles/cm}^3$, thus minimizing the opportunity for APE from PAH vapors adsorbed on particle surfaces.
- (2) The PAH analyzer did show a response to pure NaCl aerosol. The exact mechanism for this response is presently uncertain; one possible origin of the observed response is APE from trace organics (other than PAH) in the bulk NaCl used to generate the aerosol. The high-purity, reagent-grade NaCl used was, however, muffled for 4 hours in a furnace at 400°C prior to use in the experiments.
- (3) In the presence of ETS, the PAH concentrations calculated from the PAH analyzer's average responses were approximately four times (4X) higher than the fine particle ($< 2.5 \mu\text{m}$) PAH concentrations derived from integrated sampler-GC/MS measurements. In the absence of ETS, the calculated concentration from the PAH analyzer's average response was similar to the fine particle PAH concentration in one test but was only one-third of the fine particle PAH concentration in the other test. The average responses of the analyzer were converted to PAH concentrations for these comparisons using the manufacturer's suggested calibration constant of $3,000 \text{ ng/m}^3$ per pAmp of analyzer signal. It was also observed from the tests that the analyzer yielded a larger unit response to PAH in ETS than to PAH in non-ETS indoor aerosol.
- (4) The PAH analyzer provided a real-time ($< 5 \text{ sec}$) response that was proportional to indoor particulate-phase PAH. The response factors relating instrument signal to actual fine particle PAH concentration ap-

pear to vary with the nature of the indoor aerosol being sampled.

Based on these results, the following major recommendations were developed:

- (1) The origin of the observed response of the PAH analyzer to non-PAH aerosols is of considerable importance and must hence be understood. A plausible explanation for this phenomenon is that of APE from trace species, such as organics, other than PAH. However, the identity of these species is not clear at the present time and hence it is difficult to speculate on the possibility of APE from these or similar organic species adsorbed on indoor aerosols. Several tests to determine if the response is indeed due to trace organic species could be conducted, and the identity of these species could be isolated.

If the response of the PAH analyzer to non-PAH aerosols is indeed due to the trace organic species, the extent to which these species would be present in indoor aerosol must be determined. If possible, the analyzer's background response when sampling different types of indoor environments must be estimated so that background corrections can be made depending on the particle number concentration in the air sampled.

- (2) Another issue that must be addressed is the need and function of the low-voltage electrofilter used in the PAH analyzer. In the current operating mode, the electrofilter is removing gaseous ions as well as a small fraction of the charged aerosol. However, removing a portion of the charged fraction of the sampled aerosol may result in the removal of a possibly significant portion of the particulate PAH in the air. This effect may be significant for combustion aerosols that may be highly charged immediately after production. On the other hand, sampling an initially positively or negatively charged aerosol could interfere with the measurement of APE from adsorbed PAH. The need for the electrofilter must thus be studied and the impact of removing the electrofilter on instrument performance investigated.
- (3) The application of the PAH analyzer to indoor air can be addressed once the above issues have been

investigated and resolved. A series of comparison tests between integrated samplers and the PAH analyzer can be conducted to correlate the analyzer response to PAH concentration under various indoor air conditions. The response factors

determined from such tests would be beneficial to the potential application of the analyzer as an indoor air screening or monitoring tool. The PAH analyzer could also be used to measure PAH aerosol size distributions, both for the most common

combustion sources and in different indoor environments. We also recommend investigating the application of the PAH analyzer for monitoring indoor particulate-phase nitro-PAH.

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Nancy K. Wilson is the EPA Project Officer (see below).

The complete report, entitled "Evaluation of a Gossen, GmbH Model PAS 1001i Photoelectric Aerosol Sensor for Real-Time PAH Monitoring," (Order No. PB97-147938; Cost: \$21.50, subject to change) will be available only from:

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