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ABSTRACT The denuder surfaces of the gas and particle (GAP) sampler (developed at the Atmospheric Environment Service of Environment Canada) have been modified by coating with XAD-4 resin, using techniques developed at Lawrence Berkeley National Laboratory (LBNL) for the lower capacity integrated organic vapor/particle sampler (IOVPS). The resulting high capacity integrated organic gas and particle sampler (IOGAPS) has been operated in ambient air at 16.7 L min^{-1} for a 24-hour period in Berkeley, California, USA. Simultaneous measurements were made at the same collection rate with a conventional sampler that used a filter followed by two sorbent beds. Gas and particle partition measurements were determined for 13 polycyclic aromatic hydrocarbons (PAH) ranging from 2-ring to 6-ring species. The IOGAPS indicated a higher particle fraction of these compounds than did the conventional sampler, suggesting that the conventional sampler suffered from "blow-off" losses from the particles collected on the filter.

Key Words: Airborne particulate matter, denuder, gas and particle partition, phase distribution, sampling artifact, semivolatile organics

INTRODUCTION

The partitioning of polycyclic aromatic compounds (PAC) between the gas and particle phases in the atmosphere is assuming an increasingly important role in atmospheric transport models and in the assessment of the impact of PACs on human health. The traditional high volume sampler (HVS), which comprises a filter and a backup adsorber, has been shown to be subject to both positive and negative artifacts[1-7]. Positive artifacts (higher measured concentrations in the particle phase) occur when the PAC in the vapor phase are trapped by the filter substrate or the collected particles. Negative artifacts (lower measured concentrations in the particle phase) occur when the PAC adsorbed on the surface of particles leave the particles and are re-entrained in the air flow through the filter and are subsequently trapped by the adsorbent downstream of the filter. Under typical sampling conditions, the negative artifacts appear to dominate the HVS and, as a result, the HVS gives rise to gas/particle ratios for the PAC which are biased toward the vapor phase[3,8,9]. The semivolatile PAC are the most seriously affected.

Alternatives to the HVS have been investigated. These include electrostatic precipitators[10], denuders[3,4,7,11-19] and gas/gas extraction systems[20]. The GAP sampler [4,11,12] was developed over a decade ago and has been utilized in numerous field measurement programs, particularly for chlorinated aromatic compounds. The GAP sampler comprises two sampling trains: train A includes a 10 µm size selective inlet, a 6 channel, multi-annular diffusion denuder, a filter and backup adsorbers to collect any "blow-off" from the filter; and train B, which is identical to train A except that there is no denuder. The outermost channel of the denuder of train A has an outside diameter of 5.9 cm and is 70 cm long. The inner and outer walls of each channel are coated with silicone oil and crushed Tenax. Train A yields the particle phase via the filter and backup adsorber. Train B yields a measure of the total PAC material in the air. Because the trapped vapor phase material cannot be quantitatively removed from the silicone oil/crushed Tenax coating of the denuder in the GAP sampler, the vapor phase is determined as the difference between trains B and A.

Recently, a new denuder has been developed at the Lawrence Berkeley Laboratory[15]. Originally developed for PAC in environmental tobacco smoke (ETS), the coating used on the IOVPS is particularly efficient for PACs. Its major advantage is that the denuder section can be extracted and analyzed to yield a direct measure of the vapor phase concentration. The IOVPS denuder has about 50 times lower capacity than the GAP sampler and typically operates at 10 L min^{-1} for up to 3 hours. In order to combine the best features of each system and to simplify the gas/ particle sampling for PAC, we began a collaborative effort to merge the GAP and IOVPS samplers into a single, more effective denuder based sampler for the gas/particle partitioning of atmospheric PACs. We call the new sampler the integrated organic gas and particle sampler (IOGAPS).

EXPERIMENTAL

Modification of the GAP sampler denuders

The first stage in merging the two samplers involved the modification of the GAP denuder assembly to accept the XAD-4 coating used in the IOVPS. Each tube in the GAP denuder had to be sandblasted both inside and outside before the XAD-4 could be applied to the denuder's surfaces. To determine the optimum carborundum grit size for the glass blowing, several discs of

Pyrex glass were ground with a variety of grit sizes ranging from #80 to #600. The ground discs were then coated with XAD-4 and weighed on a Cahn Model 25 Automatic Electrobalance. Consistently, the highest coating was achieved on the disc sandblasted with the #320 grit. The denuders were sandblasted at LBNL with this grit size. Typical track width for #320 is 50 μm.

Preparation of the XAD-4 and denuder coating procedure

The XAD-4 was prepared as described by Gundel *et al.*[15] The coating procedure[15] for the IOVPS denuders (30 cm in length) was modified for the much longer (65 cm) GAP denuders. A Teflon lined cap was placed on the exit of the denuder and a slurry of ground XAD-4 (3.2 g in 450 mL hexane, sonicated for 10 min) was poured into the denuder until the slurry level rose above the top of the internal tubes. After capping the top end of the denuder, the entire denuder was inverted ten times so that the slurry coated all of the internal glass surfaces of the denuder. The slurry was then poured out of the denuder into a 600 mL beaker and re-sonicated for further use. A stream of nitrogen was passed through the denuder to assist in removing the solvent. When dry, the denuder was again capped and the slurry was poured back into the denuder. The denuder was coated in like manner 4 more times. When the coating process had been completed, the denuder was capped at both ends until use.

Field Testing

Preliminary field tests were carried out in early April, 1995, at LBNL on a hillside, 15 m away from a roadway. The ambient temperature ranged from 6.1 °C to 20.9 °C. Two IOGAPS were co-located, and each was installed as train A in a GAP sampler housing. One sampler served to collect the sample for 24 h at 16.7 L min^{-1} while the other provided blanks. Unground, cleaned XAD-4 was used as the backup adsorbent. Two adsorbers were used in tandem to check for breakthrough and, in each adsorber, there was approximately 5.5 g of XAD-4. Train B of each GAP unit was used for the conventional sampler. Particles were collected on Teflon-coated glass fiber filters that had been precleaned by sequential sonication in dichloromethane and methanol. The filters were weighed before and after sampling on the electrobalance to determine the mass of the collected particulate matter.

Extraction and Analysis of the Modified denuders

Due to the large size of the IOGAPS, the denuder extraction process described by Gundel *et al.*[15] had to be modified. Into the denuder, which was supported vertically in a fumehood, was poured about 500 mL of cyclohexane which had been heated to 45-50°C. 770 ng of d_{10}-fluoranthene and 570 ng of d_{10}-phenanthrene in cyclohexane were added to the denuder as internal standards to correct for any losses during sample workup. The denuder was capped and inverted 30 times (the so-called "mouthwash" technique). The extract was filtered through a Teflon filter (0.5 μm pore size) into a 1000 mL round bottom flask. The extraction was repeated with a 400 portion of warm cyclohexane. The filter was washed with 5 mL of cyclohexane, and 3 mL of hexane were added before reduction of the solvent volume to 1 mL by rotary evaporation under moderate vacuum. Each extract was subject to cleanup on a 500 mg silica solid-phase extraction (SPE) column using the procedures described by Gundel *et al.*[22]

The particulate-loaded filters were extracted by sonication for 15 min in two 3.5 mL aliquots of cyclohexane at 70 °C. Deuterated fluoranthene and phenanthrene (20 ng each) were used as internal standards. The sorbents were extracted by sonication in two 80 mL aliquots of cyclohexane at 45 °C for 25 min (each aliquot). Deuterated fluoranthene and phenanthrene (300 ng each) were used as internal standards for the sorbent beds. The extracts were filtered, reduced in volume and subject to cleanup on silica.[22]

After solvent change to acetonitrile[22], the extracts were analyzed by high performance liquid chromatography (HPLC) using the dual-fluorescence method described by Mahanama *et al.*[21] and by Gundel *et al.*[22] An Hewlett-Packard Model 1090 M HPLC instrument was used with a Vydac 201TP52-15 cm microbore column. The injection volume was 5 μL. The lower limits of detection and quantitation limits have been reported by Gundel *et al.*[15]

RESULTS

One of the sampling trains of the GAP sampler was used as the IOGAP and the other was the conventional filter-sorbent bed sampler. Because all components of the GAP sampler, including the denuder, could be quantitatively extracted for the PAC collected, we had the opportunity to compare the efficiency of the high-capacity XAD-4 coated denuder with a conventional sampling system. The denuder of the IOGAP retained the gas phase PAC whereas the filter and two downstream adsorbers yielded the particle phase. For the conventional sampling train (without denuder) the total PAC was determined by adding the material collected on the filter and that collected on the adsorbers. Apparent particle phase loading was assessed from the filter of the conventional side, and the apparent gas phase concentrations were determined from the sum of the PAH in the downstream adsorbers. Table I shows the blank-corrected results for both sampling sides of the modified GAP sampler.

A number of interesting observations arise from the data. In most cases, the total PAC detected in the IOGAP (denuder + filter + two adsorbers) matched that in the conventional side (filter + two adsorbers). The result for naphthalene was remarkably close showing 139 ng m^{-3} on the denuder side and 140 ng m^{-3} on the conventional side. For the other PAC, the agreement was not as good, but, for concentrations in the sub-ng m^{-3} range, the agreement (±10 percent) was still considered to be quite acceptable. The concentrations of phenanthrene and benz(a)anthracene in the blank denuder were greater than in the exposed denuder. High apparent blank concentrations of phenanthrene and benz(a)anthracene may be due to interference from aromatic impurities in the XAD-4 coating. Phenanthrene is a known impurity in the manufacture of polystyrene-divinylbenzene polymeric resins such as XAD-4. Further cleaning of the coating may be necessary for future use. An alternative is to use, as starting material, a purer type of polystyrene-divinylbenzene resin.

For PAC of 5 or more rings, the entire mass of the compound was found on the filter. For these compounds, the agreement between the IOGAP and the conventional sampler was better than 80%. A true measure of the agreement between samplers will have to wait proper statistical treatment of many more samples.

Comparison of the results for the two samplers showed that the apparent partitioning of PAC between gas and particle phases was dependent on the sampler type. The percentage of individual PAC in the gas phase was lower for the IOGAP. For most of the lower molecular weight PAC, the difference was a matter of a few percent; however, for the semivolatile PAH such as anthracene and fluoranthene, the difference was dramatic. For the 5-ring and higher PAH, all measurable material was found on the filter in both samplers. The above results strongly support the contention that "blow-off" of PAH adsorbed on particles is a significant loss mechanism for the semivolatile PACs. Lewis *et al.*[8,9] have found similar results with a different denuder system which was compared to the PS-1 sampler.

The results, though small in number, indicate that the engineering design of the GAP sampler and the coating procedures of the IOVPS have resulted in a high efficiency, high capacity denuder sampler, the IOGAP. Because its PAC can be determined from the denuder section, it yields a direct measure of the gas phase component of the PAC. This should result in more accurate gas/particle partition measurements for PACs.

SUMMARY

The engineering design of the GAP sampler has been successfully merged with the special denuder coating procedures developed for the IOVPS at LBNL. The resulting integrated organic gas and particle sampler has been used to collect and to determine PAC in ambient air in Berkeley, California. The first results from the IOGAP sampler are consistent with the findings of other workers who have shown that gas/particle partition measurements of semivolatile PAC made with conventional samplers are likely to be influenced by sampling artifacts due to the "blow-off" of particle-associated PAC. We are planning a more extensive field measurement program to obtain a statistically valid data set to compare the IOGAP system with a conventional sampler.

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TABLE I PAC extracted from the Denuder side of the GAP sampler.

	DENUDER SAMPLER Total particulate mass 16.7 µg/m^3						CONVENTIONAL SAMPLER Total particulate mass 16.9 µg/m^3				
PAC	Denuder ng m^{-3}	Filter ng m^{-3}	Sorbent ng m^{-3}	Sorbent ng m^{-3}	Total ng m^{-3}	Gas Phase %	Filter ng m^{-3}	Sorbent ng/m^3	Sorbent ng m^{-3}	Total ng m^{-3}	Gas Phase %
Naphthalene	126	0.008	6.9	6.31	139	90.6	0.023	134.2	5.39	140	99.98
1-Methylnaphthalene	36.2	0.004	0.40	0.014	36.6	98.9	0.009	31.3	0.137	31.4	99.97
2-Methylnaphthalene	64.7	<0.005	0.39	0.545	65.6	98.6	0.008	42.6	0.178	42.7	99.98
Acenaphthene	0.98	<0.002	0.023	0.049	1.05	93.3	<0.002	0.701	0.015	0.716	99.72
Phenanthrene	----^{1}	0.052	0.028	0.745	>0.8	----^{2}	0.036	2.145	0.158	2.34	98.46
Anthracene	0.094	0.001	<0.02	0.001	0.116	81.0	0.001	0.139	0.003	0.143	99.30
Fluoranthene	0.827	0.24	<0.03	0.171	1.27	65.1	0.030	0.250	0.117	0.397	92.44
Pyrene	0.91	0.011	<0.05	0	0.971	93.7	0.027	0.127	0.070	0.224	87.95
Benz(a)anthracene	----^{1}	0.023	0.001	0.042	>0.066	----^{2}	0.033	0.005	0.003	0.04	17.5
Benzo(b)fluoranthene	----^{3}	0.027	----^{3}	----^{3}	0.027	0	0.0205	----^{3}	----^{3}	0.0205	0
Benzo(k)fluoranthene	----^{3}	0.0067	----^{3}	----^{3}	0.0067	0	0.0169	----^{3}	----^{3}	0.0169	0
Benzo(a)pyrene	----^{3}	0.0197	----^{3}	----^{3}	0.097	0	0.0236	----^{3}	----^{3}	0.0236	0
Benzo(ghi)perylene	----^{3}	0.0397	----^{3}	----^{3}	0.0397	0	0.0504	----^{3}	----^{3}	0.0504	0

[1] The value of the blank exceeded that of the sample.

[2] Not Determined

[3] Not Detected