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AIRBORNE SAMPLES: SOLID PHASE EXTRACTION

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Introduction

Organic material in the atmosphere may exist in either the gas phase or in particles. For the purposes of this chapter, atmospheric organic material will be divided into three classes, defined by the phase distribution of the organic material in the atmosphere. Gas phase compounds will include those organic compounds which are present only in the gas phase. This will include essentially all non-aromatic organic material with fewer than about 12–14 carbon atoms. Nonvolatile organic material will include those compounds which are present in particles and whose concentrations in the gas phase are negligible compared to the particulate material. Semi-volatile organic material includes those compounds which are present in equilibrium between the gas and particulate phases in the atmosphere and for whom the concentrations in both phases are significant. The collection of gas phase and nonvolatile organic material is relatively straightforward. However, the accurate determination of the phase distribution of semi-volatile organic material requires the use of diffusion denuder technology.

Correct assessment of the contribution of fine particulate carbonaceous material to various atmospheric processes is dependent on the accurate determination and characterization of fine particulate organic material as a function of particle size. Several studies have shown that about one-third of the mass of fine particulate matter (dia. <2.5 μm) collected on filters in remote desert regions of the Southwest U.S. is organic compounds and elemental carbon. Similar fractions of carbonaceous material are found in particles collected on filters in western urban areas. In the eastern United States sulfate is the major component of filter collected airborne fine particles. However, organic material comprises one-fourth or more of the fine particulate mass. In the Northwest, organic material has been found to be the dominant fine particulate component. However, unless proper sampling procedures are used to collect particulate material, the composition of organic material in fine particles will be significantly underestimated due to losses from the semi-volatile particulate organic fraction during sample collection, i.e. a 'negative' sampling artifact.

Several studies have also indicated the presence of a ‘positive’ artifact in the determination of particulate organic compounds collected on a quartz filter, due to the adsorption of gas phase organic compounds by the quartz filter during sampling. Data obtained using sampling systems with two quartz filters in series suggest that quartz filters collect at least some gas phase organic compounds. In addition, particulate material collected on a filter can also absorb some gas phase organic compounds. The adsorption of organic compounds by a second quartz filter has been shown to be reduced, but not eliminated, in samples collected in the Los Angeles Basin if a multi-channel diffusion denuder with quartz filter material as the denuder collection surface precedes the quartz filters. This artifact can be eliminated by the use of activated charcoal at the denuder surface. Recent experiments have shown that the quartz filter artifact can result both from the collection of gas phase organic compounds and from the collection of semi-volatile organic compounds lost from particles during sampling. Thus, results available to date suggest that both a ‘positive’ and a ‘negative’ artifact can be present in the determination of particulate phase organic compounds using two tandem quartz filters.

Collection of Gas Phase Organic Material

A well validated technique for the collection of gas phase organic material for subsequent analysis is the use of SUMMA stainless steel canisters. If the canisters are properly cleaned before use and analysed within a few weeks of sample collection, valid results can be obtained for most gas phase compounds.

A second method which has frequently been used to collect gas phase organic materials consists of the use of a filter to remove particulate material, followed by a sorbent bed to collect the gas phase organic compounds. This approach is not valid if (1) the gas phase organic material is oxygenated or polar and therefore capable of being absorbed by a quartz filter or by organic material colleted by the particle removing filter, or (2) the gas phase organic material is semi-volatile and therefore, may be present on and lost from particles during sampling (see following section). The absorption of organic material by various types of filters has been reviewed. Teflon has been suggested to be relatively inert to absorption artifacts, but this filter is not amenable to the determination of total carbon. Glass fibre and cellulose membrane filters both absorb significant quantities of gas phase organic material. Quartz membrane filters are suitable for the determination of total carbon, but they also can absorb significant quantities of gas phase organic material. This is illustrated in **Figure 1** which shows the analysis of total carbon for a filter which was preceded and not preceded by a charcoal based diffusion denuder to remove gas phase material. The large peak seen in the absence of a diffusion denuder is gas phase organic material collected by the quartz filter. A similar peak (plus some higher temperature material) is seen on a second quartz filter which is not preceded by a denuder.

Materials which have been validated as sorbents for the removal of gas phase organic compounds include polyurethane foam (PUF), poly(oxy-m-terphenyl-2′,5′-ylene), Tenax, copolymers of styrene and divinylbenzene (XAD), Chromosorb and charcoal. Of these sorbents, Tenax is best suited for the collection of very low molecular weight organic material and Chromosorb or XAD are effective for collection over a wide range of molecular weights. A caution is that many of the sorbents can produce spurious results due to reactions during sample collection and each of the sorbents can be difficult to clean for the detection of trace substances. Thus, for example, a PUF cartridge produces mutagenic compounds upon extraction with methanol and Tenax forms decomposition products during sampling.

Collection of Non-Volatile Organic Material

Compounds which are sufficiently volatile that they exist essentially only in the gas phase can be collected on any filter suitable for total particle collection, such as quartz or Teflon filters. Quartz filter are usually used when the determination of total carbonaceous material in addition to the identification of specific compounds is desired. However, if only specific compound identification is desired, the use of Teflon filters avoids the complication associated with the absorption of gas phase material by the filter. However, if the target species include compounds which are reactive or unstable, they may be altered by chemical reactions associated with the sampling process. Examples of potential problems are given in the following sections.

Collection of Semi-Volatile Organic Material

To address the issues of both ‘positive’ and ‘negative’ artifacts in the sampling of particulate phase organic compounds, several groups have constructed and tested sampling systems employing diffusion denuders, filters and sorbent filters. The data obtained to date with these sampling systems show that particulate

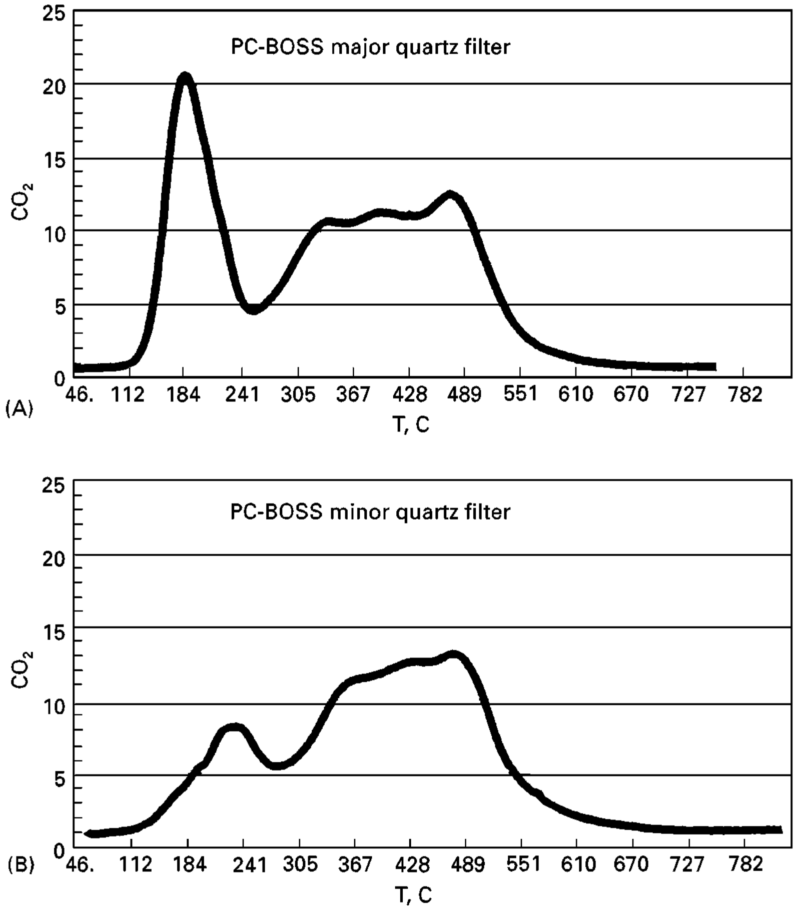

Figure 1 Temperature-programmed volatilization analysis of quartz filters (A) not preceded and (B) preceded by a denuder with charcoal impregnated filter surfaces. The large initial peak seen in (A) but not in (B) is due to the absorption of gas phase organic material by the quartz filter not preceded by a diffusion denuder to remove gas phase organic compounds.

phase organic compounds have been significantly underestimated by the collection of particles with only a filter. The collection of gas phase compounds by a quartz filter may produce a significant ‘positive’ artifact (**Figure 1**), but a much larger negative error usually results from the loss of 20–80% of the particulate phase semi-volatile organic material during sampling. This sampling artifact must be considered in the collection of semi-volatile particulate organic compounds. Accurate collection procedures for semi-volatile organic compounds must meet the following two criteria:

1. Organic compounds initially present in the gas phase which can be adsorbed onto particles or the filter must be distinguished from semi-volatile organic compounds lost from particles during sampling.
2. Organic compounds initially present in the particulate phase and lost from particles during sampling must be captured during sampling separate from compounds which are present in the gas phase in the atmosphere.

These two criteria cannot be met by any sampling procedure in which the particulate phase organic compounds are collected before the collection or separation of gas phase organic compounds because the gas phase organic compounds and organic compounds volatilized from particles become indistinguishable. Thus, it is necessary first to remove the gas phase organic compounds and then to collect the particulate phase organic compounds with a sampler which will collect all organic material, gas and particle. This can be accomplished using diffusion denuder sampling technology.

The BOSS and BIG BOSS Diffusion Denuder Samplers

Diffusion denuder sampling systems for the determination of total fine particulate organic material have been developed at Brigham Young University.

The objectives which guided the development of these sampling systems were:

1. The sampling system should have a flow rate sufficient to enable measurement of low concentrations of particulate carbonaceous material and to allow the detailed chemical characterization of particulate organic material, e.g. flow rates of from 30 to 300 L min^{-1} were considered desirable.
2. The sampler should have a diffusion denuder capable of removing all gas phase semi-volatile organic compounds which are in equilibria with compounds in the particulate phase in the atmosphere.
3. The diffusion denuder of the sampler should be effective in removing all gas phase compounds which can be adsorbed by a quartz filter or by collected particles during sampling.
4. The capacity of the diffusion denuder for the removal of gas phase organic compounds should be high enough that samples can be collected at the target flow rates over sampling periods of several days to weeks.
5. Particle losses during the passage of sampled air through the diffusion denuder should be small.
6. The sampler after the diffusion denuder should collect both particles and any semi-volatile organic material lost from particles during sampling with high efficiency.
7. The collection materials used in the sampler should be compatible both with the determination of total carbonaceous material and with the detailed chemical characterization of particulate organic material.

The BOSS (BYU Organic Sampling System) requires two different samplers as shown schematically in **Figure 2**:

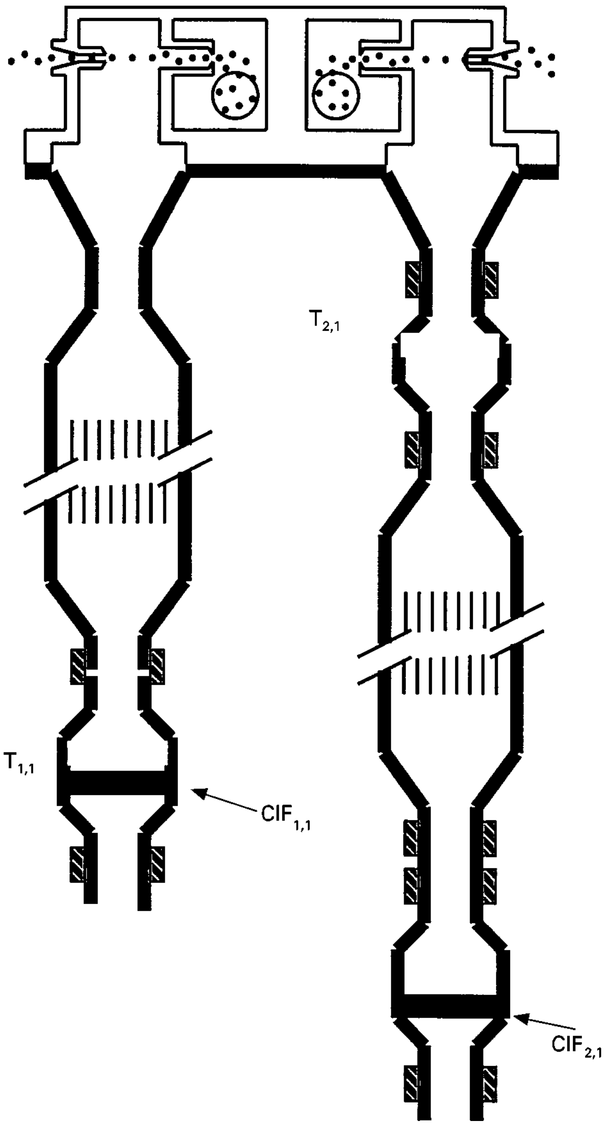

Figure 2 Schematic of the BOSS. Non-volatile particulate carbonaceous material is determined from analysis of $T_{1,1}$. Semi-volatile carbonaceous material lost from particles is determined from analysis of $CIF_{1,1}$, corrected for the denuder inefficiency determined from analysis of $CIF_{2,1}$.

1. A charcoal impregnated filter (CIF), multi-channel, parallel plate diffusion denuder followed by a filter pack containing quartz and CIF filters. The denuder removes gas phase organic compounds. The quartz filter after the denuder collects fine (<2.5 μm) particles. The organic compounds collected by the CIF sorbent filter in this sampler are semi-volatile organic compounds lost from the particles during sampling and a small fraction (about 5%) of the gas phase organic material not collected by the diffusion denuder.
2. A quartz filter followed by a CIF diffusion denuder and a CIF sorption filter. The quartz filter collects particles and any gas phase organic compounds which can be absorbed by quartz, both those originally in the gas phase and those lost from the particles during sampling. The denuder then removes gas phase compounds passing the quartz filter. Any gas phase compounds not removed by the denuder are then collected by the CIF sorbent filter. This system is used to determine independently the gas phase organic compounds not collected by the denuder to correct the data obtained with the CIF filter of Sampler 1.

The various 47 mm diameter filters of the BOSS are contained in Teflon filter packs (University Research Glass, Model 2000-30F) with the filter packs holding the quartz filter in Sampler 2, Figure 2, being modified so that the outlet is identical to the inlet to allow for convenient connection to the diffusion denuder (University Research Glass, Model 2000-30FB). The diffusion denuder is based on a design originally reported by Fitz (1990). Each denuder is comprised of 17 (4.5 × 58 cm) strips of Schleicher and Schuell charcoal impregnated filter paper which are separated at the long edges by 2-mm rods. The multi-parallel plate array of filter strips is contained within a (5 × 5 cm) square aluminium tube. The entire assembly is nominally 90 cm in length to accommodate 58 cm sorbent filter strips and two nominally 15 cm long flow straightening sections ahead of and behind the denuding section. The multi-channel diffusion denuder is designed to have acceptable efficiency for the removal of gas phase organic material in the denuder, negligible loss of particles to the denuder during sampling, and high capacity for the collection of gas phase organic material. The total capacity of the CIF multichannel denuder has not been directly measured. However, no degradation of the efficiency of the denuder for the collection of gas phase organic compounds was seen during continuous operation at 40 L min^{-1} for over two months or for sampling at 180 L min^{-1} for continuous periods equivalent to seven and fourteen days in the Los Angeles Basin, for ten days in the Mohave Desert, or for twelve days at Research Triangle Park, NC.

The CIF (Schleicher and Schuell, Inc.) strips in the diffusion denuder are used as received from the manufacturer. The 47 mm CIF (Schleicher and Schuell, Inc., No. 508) filters are cleaned with dichloromethane and dried at 200°C before use. Alternately, a 47 mm Carbon EMPORE (3M) filter may be used. The Carbon EMPORE filters may be used as received from the manufacturer, however, flow through these filters is limited to about 7 L min^{-1}. The 47 mm quartz filters (Pallflex, 2500 QAT-UP) are pretreated by firing at 800°C for four hours prior to sample collection. The flow through the two samplers of the BOSS, **Figure 2**, is controlled at about 40 L min^{-1}. A version of the BOSS using a shortened denuder (27 cm CIF strips) with a flow of from 4 to 20 L min^{-1} has also been described. The CIF or Carbon EMPORE filters may also be replaced with an XAD sorbent bed. The XAD (Rohn & Haas) is cleaned by first sonicating 10 times with CH_3OH to remove very fine particles and then Soxhlet extracting for 24 hours sequentially with CH_3OH, CH_2Cl_2 and $C_2H_5OC_2H_5$.

The efficiency of removal of gas phase organic compounds by the CIF denuder (or by an annular denuder configuration) is described by eqn [1]:

$$C/C_o = 0.819e^{-22.5(D_jLW/4Fd)} \quad [1]$$

where C_o and C are the concentrations of organic compounds entering and exiting a section of the denuder, respectively, D_j is the diffusion coefficient of the gas phase organic compound(s) at the experimental conditions, L and W are the length and effective width of the denuder section, F is the flow and d is the space between the denuder surfaces. A plot of the log of the amount collected in equal length sections of a denuder versus the distance from the start of the denuder through the section should be linear with a slope of $-22.5\ D_jW/4Fd$. The expected deposition gradient was observed for organic material collected by a CIF based denuder containing two parallel sheets of the charcoal impregnated filter material. The slope of the line describing the deposition pattern for the collection of ambient gas phase organic compounds gives an average diffusion coefficient for the collected gases of 0.052 ± 0.008 cm^2 s^{-1}. This diffusion coefficient gives a calculated effective average molecular weight of 160 ± 25. This average molecular weight is consistent with the majority of the organic material which has been shown to be collected by the diffusion denuder. The deposition pattern was also consistent with the measured efficiency of the CIF denuder for the removal of gas phase organic compounds.

The importance of the particulate organic compounds which have not been identified in past studies where particles are collected on a filter will be dependent on the chemical composition and the size distribution of the particulate organic compounds, both those lost from the particles during sampling and those remaining on the particles after sampling. A high-volume, multi-component diffusion denuder sampling system (BIG BOSS) for the determination of the size distribution and chemical composition of fine particulate organic compounds using diffusion denuder sampling technology has been developed and tested.

The BIG BOSS uses a variety of size selective virtual impactor inlets to control the particle size of the particles introduced to the diffusion denuder sampler. The inlet system is a modification of a high-volume, multi-jet virtual impactor. The nominal total flow through all systems of the BIG BOSS is 0.9 m^3 min^{-1} inlet flow. This flow is divided among four systems, each with a coarse particle minor flow stream and a fine particle major flow stream. Two of the four systems have an inlet cut of 2.5 μm. The other two systems are designed to operate with an inlet cut of 0.8 and 0.4 μm (see Tang, 1994).

The PC-BOSS Denuder Sampler

The combination of the technology used in the previously described BIG BOSS sampling system and the

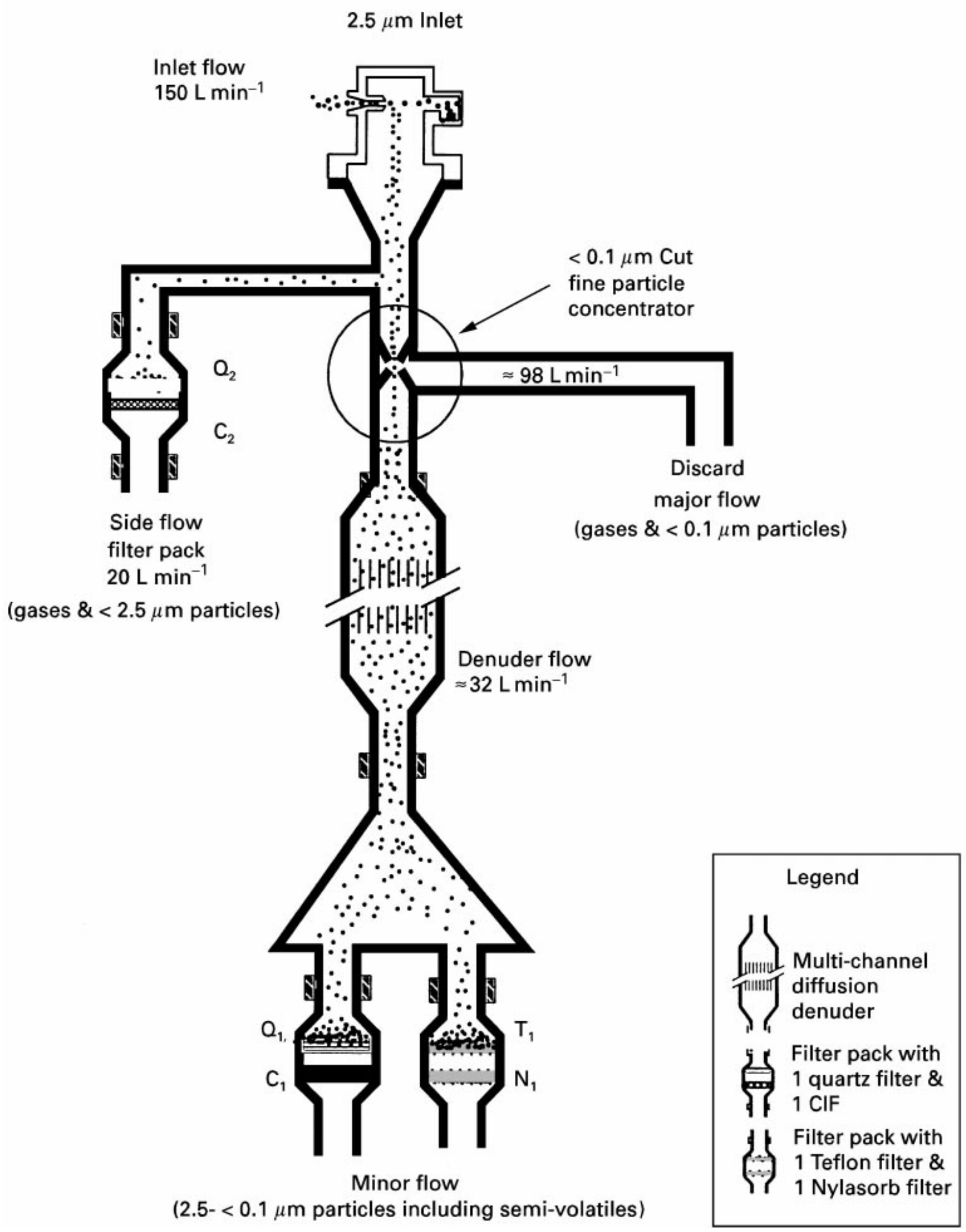

Figure 3 Schematic of the PC-BOSS. The composition of fine particulate matter is determined from analysis of the two filter packs after the denuder. The efficiency and losses of the fine particle concentrator is determined by comparison of sulfate on Q_2 with that on Q_1 or T_1.

Harvard particle concentrator results in the Particle Concentrator-Brigham Young University Organic Sample System (PC-BOSS) shown schematically in **Figure 3**. The system has been optimized to meet the following criteria: (1) removal of at least 75% of the gas phase material before the sampled aerosol is passed through the diffusion denuder, (2) efficiency, >99% for the removal of SO_2, HNO_3 and gas phase semi-volatile organic material, (3) determination of particle mass, carbonaceous material and nitrate with a diffusion denuder sampler, (4) operation on less than 20 amps of 110 V power.

The inlet to the sampler is a Bendix cyclone with a particle cut of 2.3 μm aerodynamic diameter at an inlet flow of 150 L min^{-1}. Following the inlet, 20 L min^{-1} is diverted to a filter pack to provide data for calculating the efficiency of and losses in the PC-BOSS particle concentrator. The remaining flow enters the virtual impactor particle concentrator. The design and evaluation of the particle concentrator has been previously described. The particle concentrator separates most of the gas phase material into the major flow and leaves particles larger than the cut point (about 0.1 μm) along with a significantly reduced fraction of the gas phase material in the minor flow. The performance of the particle concentrator for collection of ambient samples with the PC-BOSS was evaluated as a function of the minor to major flow ratio, and the distance between the accelerator and receiver slits of the virtual impactor. The optimum design uses a single particle concentrator with a 9.5 cm long slit and a distance between the accelerator and receiver slits 1.5 times the slit width of 0.32 mm. The minor flow (25% of the total 150 L min^{-1} flow) containing concentrated particles enters the BOSS diffusion denuder. The denuder is followed by two parallel filter packs (**Figure 3**). The filter pack containing a 47 mm quartz filter (Pallflex, prefired) followed by a 47 mm charcoal impregnated filter is used to determine fine particulate carbonaceous material, including semi-volatile organic material lost from the particles during sampling. The second filter pack contains 47 mm Teflon (Gelman Zefluor) and nylon (Gelman Nylasorb) filters to determine mass, sulfate and nitrate, including any nitrate lost from particles during sampling.

The IOVPS and IOGAPS Denuder Samplers

Researchers at Lawrence Berkeley Laboratories have developed an annular denuder sampling system, the Integrated Organic Vapour/Particle Sampler (IOVPS) with an XAD-IV based diffusion denuder for the measurement of SVOC. This diffusion denuder sampler is similar in design and operation to the BOSS systems described above. The IOVPS is shown schematically in **Figure 4**. An advantage of the IOVPS sampler is that the gas phase material collected by the denuder can be easily recovered for organic compound chemical characterization and quantitation. Current disadvantages of the sampler are the total carbonaceous material is not determinable in the denuder or post-filter XAD sorbent beds (**Figure 4**) and the capacity of the denuder limits the length of time over which the denuder may be used from hours to days.

The denuder of the IOVPS system is prepared by adhering very fine mesh XAD to a glass multi-annular denuder surface. The adhesion of the finely ground XAD to the sandblasted glass is strong enough that the coating is resistant to removal by handling, solvent washing and air sampling. Quantitation of gas phase organic compounds removed by the IOVPS denuder is accomplished by extraction with a suitable solvent and analysis by GC or GC/MS. The collection efficiency of these denuders for various gas phase organic compounds has been shown to be close to that predicted by eqn [1]. A 5-channel denuder with 1 mm spacing in the annulus and a coating length of 38 cm has been used for most applications of the IOVPS denuder.

The capacity of the IOVPS XAD based denuder is dependent on two factors: (1) the capacity of the XAD surface for a given compound and (2) the time required to elute a dilute concentration of a given gas down the XAD column length. The dominant factor appears to be the movement of collected gas phase material down the XAD column. As a result, studies using the IOVPS denuder have generally been limited to chamber studies where the sampling period is short or to ambient studies where the sample collection occurred only over a few hours. By increasing the length and surface area of the denuder (including using parallel denuders) prototype systems have been developed by Lawrence Livermore Laboratory and the Atmospheric Environment Service of Environment Canada (IOGAPS, Integrated Organic Gas and Particle Sampler) which are capable of sample collection for up to 48 hours. Comparisons of results obtained from 24 hour IOGAPS and sequential 4 hour IOVPS data where the annulus width of the IOGAPS was 1.5–3.0 mm with a residence time of 2.6 s indicated there was about 10% breakthrough of naphthalene in the IOGAPS. A redesign with an annulus width of 1.0–1.4 mm is expected to eliminate this problem.

Particle losses to the wall of the IOVPS denuder has been evaluated in several studies. The results are essentially identical to those reported above for the BOSS and BIGBOSS samplers. With face velocities of around 20 cm s^{-1} through the denuder, losses are less than 2%. At higher face velocities of 35 to 50 cm s^{-1}, the losses increase to about 5–7%. These losses are comparable to that seen for conventional annular denuders.

Other Diffusion Denuder and Related Samplers

Diffusion denuder sampling techniques have also been developed and used by several other investigators to determine fine particulate organic material. The focus of these studies has been on the determination of specific organic compounds. Krieger and Hites have used short sections of capillary gas chromatographic columns as a diffusion denuder and determined concentrations of gas and particulate phase polychlorinated biphenyl (PCB) and polyaromatic hydrocarbon (PAH) compounds. Coutant *et al.* have described the development of a circular multi-channel diffusion denuder for the study of PAH in ambient air. However, results on field studies using the sampling system have not yet been published. The

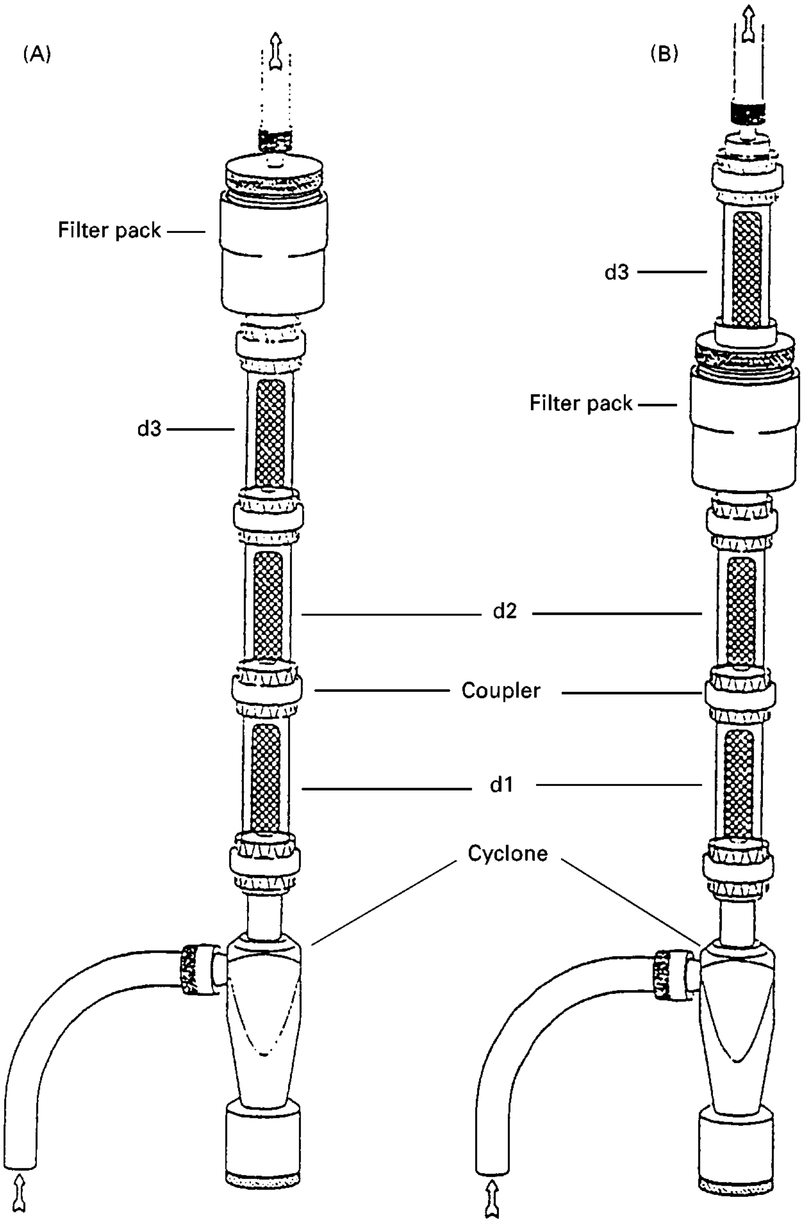

Figure 4 Schematic of the IOVAPS (from Gundel, 1999). The denuders contain XAD as the gas phase organic sorbent. Non-volatile particulate carbonaceous material is determined from analysis of the filters in either of the filter packs. Semi-volatile carbonaceous material lost from particles is determined from analysis of the denuder d3.

Atmospheric Environment Service of Environment Canada has been involved since 1984 in the development and use of a diffusion denuder sampler for the determination of PCBs and chlorinated hydrocarbons. The instrument uses a silicone gum/Tenax-coated, multi-tube, annular, diffusion denuder to remove the target organic compounds. Turpin *et al.* have developed a sampling system which corrects for the loss of semi-volatile organic compounds during sampling by removal of most of the gas phase material from the particles in a diffusion separator sampling system. The system has been evaluated for the collection of PAH. All of the systems which have been described by other research groups collect samples at a flow rate of a few L min^{-1}. One advantage of the use of the diffusion denuder sampling systems described above is that the attainable high flow rate, 200 L min^{-1}, allows for more collected material and a wider range of analyses on the collected samples.

Residence Time in the Denuder

The efficiency of a diffusion denuder sampler for the removal of gas phase material can be improved by increasing the residence time of the sampled aerosol in the denuder. However, the residence time can only be increased within limits. Since the diffusion denuder reduces the concentration of gas phase semi-volatile organic material, semi-volatile organic material present in the particles passing through the denuder will be in a thermodynamically unstable environment and will tend to outgas SVOC during passage through the denuder. The residence time of the aerosol in the denuder should be short enough to prevent significant loss of particulate phase SVOC to the denuder. Various studies have suggested that the residence time in the denuder should be less than about 2 s. The residence times in the various denuder designs described above are about 1.5, 0.2, 0.2 and 1.4 s for the BOSS (or PC-BOSS), BIG BOSS, IOVPS and IOGAPS denuders, respectively.

Changes in Chemical Composition during Sampling

The preceding sections have outlined sampling systems designed to identify correctly the atmospheric gas and particulate phase distribution of collected organic material. An additional sampling artifact which has been little considered in the collection of atmospheric sampling is the potential alteration of organic compounds as a result of the sampling process. These alterations appear to result from the movement of ambient air containing oxidants and other reactive compounds past the collected particles. The addition of NO_2 (<1 p.p.m.) or O_3 (<200 p.p.b.) to the sampled air stream (0 to 5°C) for a high volume sampler reduced the concentrations of benzo(a) pyrene and benzo(a)anthracene from a few up to 38%, with the observed reduction increasing with increased concentration of the added gases. Spiking a filter with an amine resulted in an increase in measured concentrations of nitrosoamines in both the filter and a following XAD sorbent bed for a mid-volume sampler. Similar results have been obtained for the exposure of a deuterated amine on a filter to NO_x. When Tenax columns spiked with deuterated styrene and cyclohexane were exposed to p.p.m. concentrations of ozone or halogens, oxygenated and halogenated compounds were shown to be formed. Similar oxidation of aldehydes and PAN during sampling has been observed. Collected PAH compounds can be oxygenated and/or nitrated on a filter but 1-nitropyrene has been shown to be resistant to additional nitration. These various chemical transformations of collected organic compounds can be eliminated by removal of the gas phase oxidants, NO_x, HNO_3, etc., prior to collection of the particles. The PC-BOSS denuder described above should be effective in eliminating most of chemical transformation artifacts since reactive gases are removed by the charcoal denuder which precedes the particle collection filter.

Application of Diffusion Denuder Samplers to the Determination of Semi-Volatile Organic Material

The application of diffusion denuder samplers to the determination of gas and particulate phase semi-volatile organic material is illustrated with results from three different studies, one each using the BIG BOSS, PC-BOSS and IOVPS samplers.

Semi-volatile organic compounds lost from particles during sampling and subsequently collected by an XAD-II trap and semi-volatile organic compounds retained by the quartz filters during sampling have been chemically characterized for <2.5 μm particles in BIG BOSS samples collected at Azusa in the Los Angeles Basin. The XAD-II sorbent beds included significant concentrations of aliphatic, acidic and aromatic organic compounds. Similar compounds were also detected in the GC–MS analysis of the filter extracts. However, the compounds retained by the filter were of higher molecular weight. The distribution of compounds lost from particles during sampling and remaining on the particles during sampling is illustrated by the GC/MS results for paraffinic compounds (**Figure 5**).

The pattern seen in Figure 5 is typical of results obtained for all classes of compounds and all samples studied to date. For those compounds which have been characterized, the envelopes of each class of compounds remaining in the particles and lost from the particles overlap. For each compound class, the more volatile compounds predominate in the material lost from the particles and collected in the XAD-II bed during sampling. In contrast, the higher molecular weight organic compounds are retained by the particles during sampling. For example, particulate n-tetradecane and n-pentadecane are found only in the XAD-II bed and not in the particles after sampling (Figure 5). Hydrocarbons lower in molecular weight than these two compounds are found in comparable concentrations in the XAD-II beds of both Samplers 1 and 2 of the BOSS (**Figure 2**) indicating they originate mainly from the breakthrough of some fraction of the gas phase component of these species. In contrast, n-tetracosane and higher molecular weight aliphatic hydrocarbons are retained by the particles during sampling and are not found in the XAD-II sorbent beds (**Figure 5**). Compounds of intermediate molecular weight, e.g. n-decosane, are partially lost and partially retained by the particles. Also illustrated

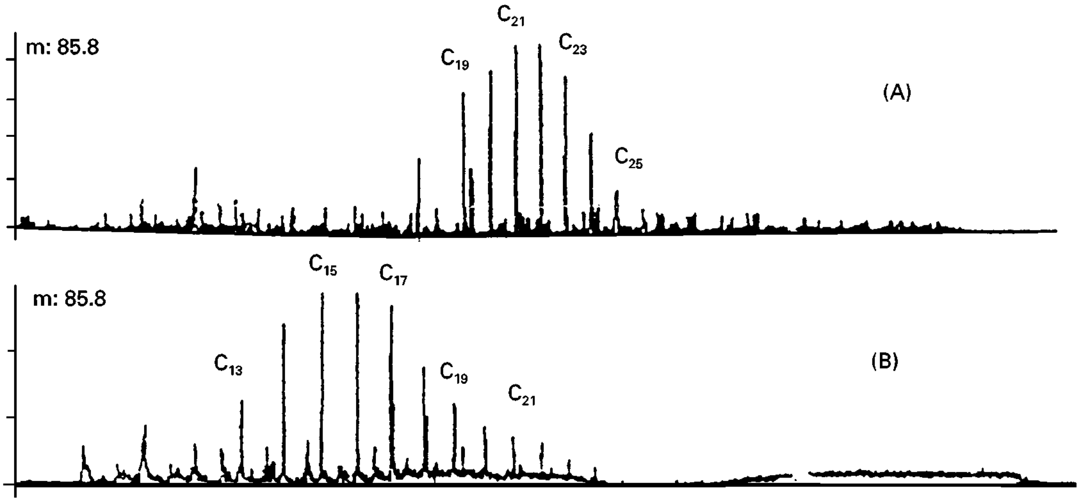

Figure 5 GC/MS data (m/z = 85) for paraffinic compounds; (A) retained by particles and (B) lost from particles during collection on a filter (from Tang, 1994).

by the GC-MS data is the increased tendency for lower molecular weight semi-volatile organic compounds to be retained by the particles during sample collection as the polarity of a given molecular weight compound increases. For example, n-heptadecane (MW 226) is largely lost from particles during sampling (**Figure 5**). However, lauric acid (MW 214) and fluoranthene (MW 202) are largely retained by the particles during sampling.

Results for the determination of PAH compounds in indoor air obtained with the IOVPS and with a conventional filter-sorbent sampler are given in **Figure 6**. As indicated in Figure 6(A), about 90% of the phenanthrene, pyrene and chrysene are present in the gas phase. However, about 60% of the more volatile phenanthrene (MW 178) and pyrene (MW 202) are lost from the filter of the filter pack during sample collection. In contrast, the loss of the less volatile chrysene (MW 228) was negligible. These results are comparable to those given above for the Azusa study with the BIG BOSS.

Recent studies have indicated that the U.S. Environmental Protection Agency (EPA) PM_{10} air quality standard does not provide adequate human health protection because the fine particle ($PM_{2.5}$) component of PM_{10} is related to observed health effects at concentrations substantially below the PM_{10} standard. As a result, EPA has promulgated a $PM_{2.5}$ air quality standard. In order to implement the new $PM_{2.5}$ standard, a Federal Reference Method (FRM) for fine particulate monitoring has been proposed (see Schaefer, 1997). The $PM_{2.5}$ FRM is a single filter pack sampling method with gravimetric determination of the collected mass.

For the reasons outlined above, the FRM will tend to not measure semi-volatile fine particulate constituents. The amount of semi-volatile material is expected to be a substantial fraction of the total $PM_{2.5}$

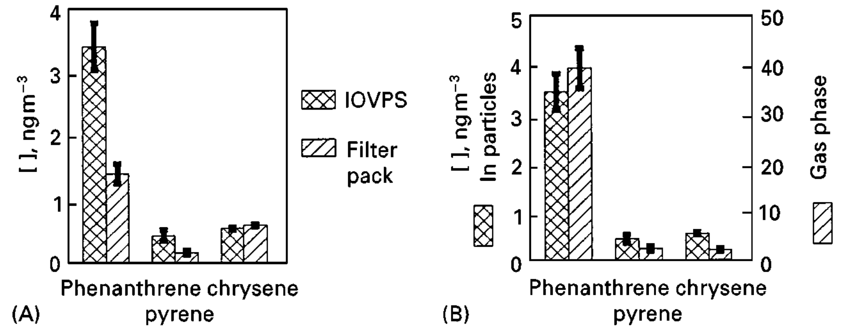

Figure 6 Retention and loss of particulate PAH compounds during sampling. (A) The lower concentrations determined by a filter pad, compared to IOVPS, is due to losses from particles during sampling. (B) Concentrations of both particle and gas phase PAH with the IOVPS.

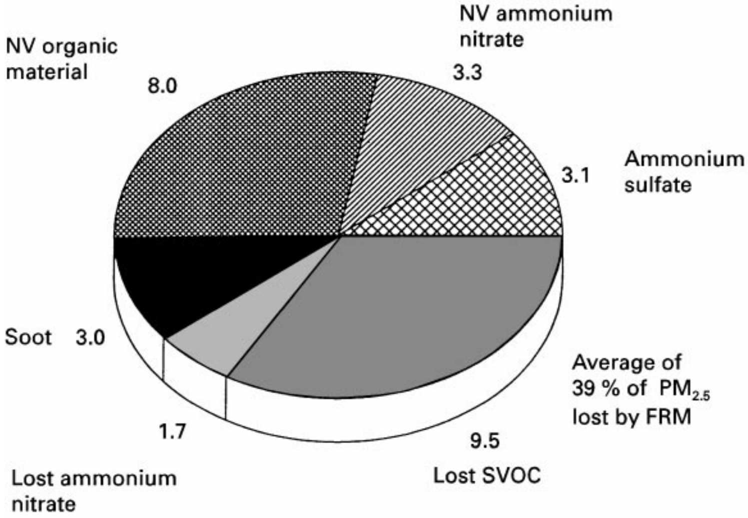

Figure 7 Average composition of $PM_{2.5}$ in Riverside CA, including semi-volatile ammonium nitrate and organic material lost during sampling from particles collected on a filter.

mass observed in many urban areas. As a result, the proposed Federal Reference Method may underdetermine fine particulate mass. A comprehensive field study to evaluate the PC-BOSS and compare with results obtained by other $PM_{2.5}$ sampling methods, including the FRM has been conducted in Riverside, California. Riverside was chosen for the study because high particulate pollution resulting from summer inversions is expected. Both annual and 24 hour maximum concentration of PM_{10} exceeded the federal standards in 1995 and high concentrations of particulate semi-volatile ammonium nitrate and organic materials are expected to be present in this area.

The average result for the determination of the composition of fine particulate matter in Riverside during August and September 1997 are given in **Figure 7**. Substantial amounts of both ammonium nitrate and semi-volatile organic material were lost from the filters of both the PC-BOSS and the $PM_{2.5}$ FRM. The average loss of ammonium nitrate (34%, 1.7 $\mu g\, m^{-3}$) was smaller than that for the semi-volatile organic material (54% of total fine particulate organic material, 9.5 $\mu g\, m^{-3}$). As a result of the loss of these species, the $PM_{2.5}$ FRM lost an average of 39% of the fine particulate material during the collection of the sample.

The results obtained in these three examples illustrate the importance of correctly sampling for semi-volatile particulate organic material.

See also: **II/Extraction:** Solid-Phase Extraction. **Membrane Separations:** Filtration. **III/Atmospheric Analysis: Gas Chromatography:** Supercritical Fluid Chromatography. **Solid-Phase Extraction with Discs**.

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ALCOHOL AND BIOLOGICAL MARKERS OF ALCOHOL ABUSE: GAS CHROMATOGRAPHY

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The use of alcoholic beverages is probably the most ancient social habit worldwide, but alcohol abuse has generated severe problems. Chronic and/or acute alcohol intoxication has been demonstrated to be connected with serious pathologies, suicides, homicides, fatal road and industrial accidents and many criminal offences. Alcoholism is a widespread social, medical and economic problem in a large section of the population of nearly all ethnic groups. Therefore, it is of great importance to have diagnostic tools (biological markers) to detect excessive alcohol consumption and alcoholism. This article deals with gas chromatographic techniques to determine excessive alcohol consumption. The following parameters are described: ethyl alcohol and congeners, ketone bodies, ethyl glucuronide, fatty acid ethyl esters and condensation products like salsolinol.

Ethyl Alcohol

The most obvious and specific test for heavy drinking is the measurement of blood, breath or urine alcohol (ethyl alcohol). However, this simple test cannot distinguish between acute and chronic alcohol consumption, unless it can be related to an increased tolerance of alcohol. According to the American National Council on Alcoholism (NCA), the first-level criteria for the diagnosis of alcoholism are blood alcohol exceeding 1.5 $\mathrm{g\,L^{-1}}$ without gross evidence of intoxication, over 3 $\mathrm{g\,L^{-1}}$ at any time, or over 1 $\mathrm{g\,L^{-1}}$ in routine examination. The determination of alcohol has already been the subject of many reviews. The most important facts are summarized here.

As a first step, various pitfalls and analytical problems such as interference in alcohol analysis induced by cleaning the skin with ethanol or isopropanol before expert venepuncture should be borne in mind. The stability of ethanol during storage is a problem. The main factors affecting alcohol determination in stored blood are the duration and temperature of storage, with negligible losses in the frozen state, and the presence of a preservative. Three mechanisms accounting for these changes are: oxidation (highly