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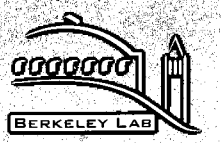

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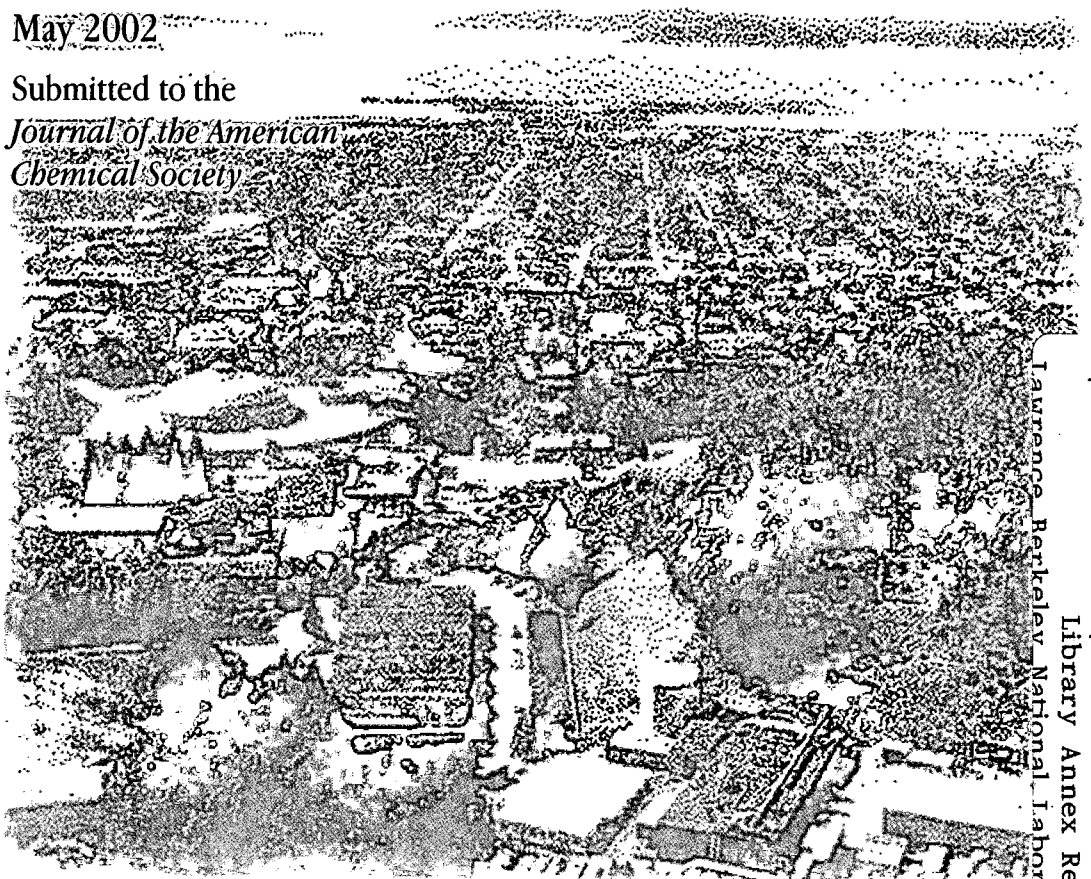

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Recovery of Semi-volatile Organic Compounds During Sample Preparation: Compilation for Characterization Of Airborne Particulate Matter

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Abstract

Semi-volatile compounds present special analytical challenges not met by conventional methods for analysis of ambient particulate matter (PM). Accurate quantification of PM-associated organic compounds requires validation of the laboratory procedures for recovery over a wide volatility and polarity range. To meet these challenges, solutions of n-alkanes (nC_{12} to nC_{40}) and polycyclic aromatic hydrocarbons PAHs (naphthalene to benzo[ghi]perylene) were reduced in volume from a solvent mixture (equal volumes of hexane, dichloromethane and methanol), to examine recovery after reduction in volume. When the extract solution volume reached 0.5 mL the solvent was entirely methanol, and the recovery averaged 60% for n-alkanes nC_{12} to nC_{25} and PAHs from naphthalene to chrysene. Recovery of higher MW compounds decreased with MW, because of their insolubility in methanol. When the walls of the flasks were washed with 1 mL of equal parts hexane and dichloromethane (to reconstruct the original solvent composition), the recovery of nC_{18} and higher MW compounds increased dramatically, up to 100% for $nC_{22} - nC_{32}$ and then slowly decreasing with MW due to insolubility. To examine recovery during extraction of the components of the High Capacity Integrated Gas and Particle Sampler, the same standards were used to spike its denuders and filters. For XAD-4 coated denuders and filters, normalized recovery was > 95% after two extractions. Recovery from spiked quartz filters matched the recovery from the coated surfaces for alkanes nC_{18} and larger, and for fluoranthene and larger PAHs. Lower MW compounds evaporated from the quartz filter with the spiking solvent. This careful approach allowed quantification of organics by correcting for volatility- and solubility-related sample preparation losses. This method is illustrated for an ambient sample collected with this sampler during the Texas Air Quality Study 2000.

Introduction

Accurate determination of airborne semi-volatile organic species presents sampling and analytical challenges because their lability complicates both collection and quantification. Improved collection is possible with new air sampling technology such as the Integrated Organic Gas and Particle Sampler (IOGAPS) that incorporates extractable sorbent-coated diffusion denuders and filters (*1-2*). However, accurate quantification of PM-associated organic compounds also requires validation of the laboratory procedures for recovery (e.g., solvent extraction and reduction of volume) over wide volatility, molecular weight and polarity ranges. It is necessary to account for losses of both a) semi-volatile compounds that can evaporate during the reduction of volume procedure and b) high molecular weight species that may precipitate during steps that were intended to lower limits of detection. Careful attention must be paid to sample preparation techniques to ensure maximum recovery of the wide variety of organic compounds that are associated with ambient particulate matter.

Previous work has led to the widespread use of organic solvent mixtures or a series of solvents to optimize extraction of airborne particulate organics. Grosjean (*3*) showed that mixtures of non-polar and polar solvents extracted more organic carbon from PM than could be removed by individual solvents. Various mixtures have been evaluated in the last two decades: Appel et al. (*4*) recommended sequential use of benzene followed by a methanol-chloroform mixture. Cadle and Groblicki (*5*) determined that a benzene-ethanol mixture minimized residual non-extractable carbon in samples of particles, compared to a variety of solvents and mixtures. Sequential extractions with dichloromethane and acetone have been used for studies of the genotoxicity of

ambient PM (*6-7*). Mazurek et al. (*8-9*) developed a multi-step solvent extraction protocol (using hexane, followed by a benzene-isopropanol mixture) that has been used extensively for speciation of organics in ambient and source particulate matter (*10-17*).

The recognition of the important role that SVOC play in PM atmospheric behavior and health effects has led to development of improved technology, such as extractable diffusion denuders, to reduce sampling artifacts while allowing determination of both gas and particulate phase SVOC concentrations. Extraction of the multi-channel XAD-coated diffusion denuders of the IOGAPS required a solvent mixture that would provide maximum solubility of adsorbed semi-volatile compounds without dissolution of the epoxy joints of the glass denuders. Based on the previous work of other investigators, experience with the IOGAPS (*1*), and the long-term goal of determining polar as well as non-polar organic compounds, we chose an extraction mixture of hexane, dichloromethane and methanol.

This study began as an effort to validate sample preparation procedures for characterization of gas and particle samples that had been collected with the high capacity (HiC) IOGAPS and related samplers. However, a more general purpose emerged with our growing recognition that insufficient attention to analyte recovery could undermine the efforts of any research team, with any sampling technology, to characterize the wide range of organics associated with PM. Thus, the broader objective is to describe the implications of these recovery results for past and future efforts to speciate airborne semi-volatile and particulate organics. The results of our quality control and quality assurance efforts broadened beyond devising procedures to optimize recovery of specific compounds to a) exploring the implications of our results for interpretation

of past efforts to characterize particulate organics and b) developing recommendations for future work by any investigators.

First, we examined how to optimize recovery of a group of non-polar alkanes and PAHs from a solvent mixture of hexane, dichloromethane and methanol after reduction of solvent volume. Next, we measured the recovery of this group of compounds from spiked HiC IOGAPS components (XAD-4 coated diffusion denuders, quartz filters and XAD-4 impregnated quartz filters), and optimized the extraction procedures. We then determined this group of compounds in a field sample from the HiC IOGAPS that operated at La Porte Airport, near Houston, Texas, during the Texas Air Quality Study – 2000 (TEXAQS-2000). Finally the implications of our results are discussed by comparison to other quantitative speciation studies, along with recommendation for future work.

Experimental Section

Overview of Sample Preparation for HiC IOGAPS

For illustration of the sample preparation method we analyzed a HiC IOGAPS (Model 3000DB, URG Corp., Chapel Hill, NC) air sample that was collected on August 31, 2000, between 00:10 and 11:30 (Local Time) during the Texas Air Quality Study, August-September, 2000, at the LaPorte Airport. Figure 1 shows a schematic diagram of the sampler. The HiC IOGAPS had a 2.5 μm cyclone for particle discrimination, followed by two 8-channel XAD-4 denuders in series (each had 52 mm outer diameter and 285 mm length), one pre-baked quartz and three XAD-4 impregnated quartz filters (90 mm diameter). The sample was collected at 85 L min^{-1} for 11.5

hours and yielded three extracts of each denuder and one extract for each filter, for a total of 10 extracts, not counting filter blanks. Figure 2 shows a flow diagram of sample preparation. Before extraction, a mixture of three deuterated PAH standards was added to each denuder. The denuders were extracted in solvent mixture of equal volumes of pesticide grade hexane, dichloromethane and methanol (Hex:$MeCl_2$:MeOH) in a laboratory at the University of Houston, Clear Lake, where the extracts were also reduced in volume and restored to the original solvent composition as described below. The 1.5 mL extracts were stored at –30°C for subsequent analysis. The filters were stored at –30°C in Teflon-sealed 50 mL pre-baked glass centrifuge tubes. The filters were thawed, extracted and analyzed at the US EPA's National Exposure Research Laboratory in RTP, NC.

Extraction details

Before use, each denuder had been given a unique identification number, coated with fine particles of XAD-4 (*18-20*), and spiked with 0.1 mL of a deuterated PAH mixture as field surrogates to monitor processing losses during sample extraction and reduction of volume. The surrogate recovery was evaluated for acceptance by determining whether the measured concentration fell within the acceptance limits of 80-120 percent. The deuterated PAH solution contained anthracene-d_{10} (0.04 $\mu g\ mL^{-1}$), phenanthrene-d_{10} (3.3 $\mu g\ mL^{-1}$) and fluoranthene-d_{10} (1.0 $\mu g\ mL^{-1}$), all in hexane, at concentrations estimated to be similar to the native airborne PAH. The denuders were allowed to dry for a few minutes until the solvent evaporated and then extracted to obtain a pre-sampling blank. After collection of the ambient sample, and before extraction, each denuder was spiked again with the same deuterated PAH mixture.

The procedure for denuder extraction follows: The denuder was sealed at one end with a clean Teflon end cap, half-filled with 125 mL of Hex:$MeCl_2$:MeOH solvent, and capped with another Teflon end cap that had a hand-tight Swagelok® fitting for pressure release. (This is an important safety measure, as freshly prepared Hex:$MeCl_2$:MeOH can release dissolved air unless it is sonicated before use.) A rolling rinse technique was used; the capped denuder was rolled back and forth along the laboratory bench top for 30 revolutions. To exclude any XAD-4 that may have shed from the denuder coating, each extract was passed through a Teflon membrane (unlaminated Fluoropore, 0.45 μm pore size, FHUP04700, Millipore Corp.) before volume reduction. The filtrate was transferred to clean 125 mL wide mouth brown bottles for temporary storage. (Glassware had been rinsed with Hex:$MeCl_2$:MeOH solvent and heated to 500°C for 2 hours.) After ambient sampling, each denuder was extracted three times, and each extract was processed separately, with the third extract serving as the denuder blank for the next use of that denuder. Quartz filters and XAD-4 impregnated quartz were each extracted twice by sonication for 1 hour at ambient temperature in 50 mL of Hex:$MeCl_2$:MeOH solvent and filtered by the same procedure as used for denuder extracts. In some cases it was necessary to re-filter the extracts with a 0.2 μm syringe filter (Acrodisc® CR PTFE) before GC-MS analysis. For ongoing efforts we recommend that deuterated surrogates be added to each filter before extraction, in the same approach as the denuders.

Reduction of Volume

During the TexAQS field study, we used a Labconco RapidVap® Vacuum Evaporation System (Model # 79000-00), which accommodated 8 (170 mL) samples, instead of a conventional rotary evaporator, because of the large number of extracts (>500). The evaporation tubes had 1.5 mL

endpoint stems with volume markings. The vacuum model was chosen rather than the N_2 model because preliminary results with the N_2 model yielded extracts that contained significant amounts of water. The water had condensed from room air during the procedure. With careful external baffling to prevent entry of ambient air, it has been possible to evaporate the Hex:$MeCl_2$:MeOH solvent with the N_2 model, without water condensation (Y. Pang, private communication.)

Before the field study, the sample preparation procedures were optimized in a stepwise fashion, with assessment of the recovery of alkanes and PAHs at each step. What follows is the optimized protocol. To test the recovery after the solvent reduction procedure, 1 mL aliquots of an n-alkane-PAH mixture (Table I) were diluted to 100 mL in Hex:$MeCl_2$:MeOH solvent. The diluted standard mixture (later, denuder or filter extract) was also spiked with 1.58 μg of the non-volatile $nC_{24}D_{50}$ (in Hex:$MeCl_2$:MeOH) as a laboratory surrogate to monitor processing losses during reduction of volume. The surrogate recovery was evaluated for acceptance by determining whether the measured concentration fell within the acceptance limits of 80-120 percent. The solution was then filtered through a Teflon membrane, transferred into a Labconco evaporation tube and reduced to ~0.5 mL using the programmed step-wise process shown in Table II. The step-wise process was necessary to prevent bumping of the solvent mixture.

When the volume reached 0.5 mL, the concentrated standard solution or sample extract was cooled and weighed while still in the evaporation tube. Density measurements showed that the solvent mixture was primarily methanol (> 99%) at this point, so that exact volumes were determined gravimetrically. Finally, to ensure dissolution of any compounds coating the walls,

before transfer, the walls of each tube were rinsed with 1 mL of equal volumes of hexane:dichloromethane (Hex:$MeCl_2$) containing the internal standard p-terphenyl-d_{14} (1.84 μg mL^{-1}) that was used later to account for variation in GC-MS injection volume. The 1.5 mL extracts were thus reconstituted into the original Hex:$MeCl_2$:MeOH solvent mixture before quantitative transfer to 1.8 mL clean glass auto-sampler vials with Teflon-lined caps.

Determination of Alkanes and PAHs

Determination *of* the alkanes and PAHs was performed using a Varian Saturn IV® gas chromatograph- ion trap mass spectrometer (GC-MS) with a SPI injection system. The GC had a 30-meter Rtx-5Sil MS column (0.28 mm ID, 0.25 μm film thickness) and a 10-meter Integra Guard column. The carrier gas was helium at a flow rate of 1 mL min^{-1}. The oven temperature was held at 60 °C for 5 minutes, heated at 10 °C min^{-1} to 140 °C, then at 5 °C min^{-1} to 320 °C, and held at 320 °C for 15 minutes. The MS was operated under the following conditions: trap temperature 225°C, emission current 15μA, scan rate 50-350 Daltons in 0.5 seconds and A/M amplitude was 3.0 Volts. The non-polar organic compounds were identified by comparison with retention times and mass spectra of authentic standards. The standard deviation for repetitive GC-MS runs was < 4%. The concentrations were normalized to the p-terphenyl-d_{14} response for each injection such that:

$$C_x = \frac{A_x \cdot RF_x}{V} \cdot \frac{C^0_{ptp}}{\frac{A_{ptp} \cdot RF_{ptp}}{V}} \qquad (1)$$

where A is the area count from the GC-MS, RF is the response factor (μg/area counts), V is the total volume of the solution (mL), C^0 is the initial concentration (μg/ml), C is the final concentration (μg/ml). The subscript x refers to any given species within the solution, and *ptp* refers to the p-terphenyl-d_{14}. The response for each n-alkane and PAH was found to be linear over the concentration range used.

Results

Optimizing recovery of alkanes and PAHs after solvent reduction and reconstitution

The possibility of cross contamination during simultaneous evaporation of multiple extracts was examined by processing four vials of the standard mixture of alkanes and PAHs (Table I) in Hex:$MeCl_2$:MeOH along with four solvent blanks. Concentrations of the target compounds in the blanks were indistinguishable from solvent blanks, and therefore we concluded that no appreciable cross contamination occurred.

Figure 3 shows the results for recovery of alkanes and PAHs for several different procedures. When the standard mixture in Hex:$MeCl_2$:MeOH was reduced to 0.5 mL without reconstitution, (open squares) recoveries varied for each species, depending on volatility, and solubility in methanol. The most labile species nC_{12} had 30% recovery. The recovery increased with MW and plateaued at 60% between nC_{16} and nC_{24}. The recoveries for the n-alkanes above nC_{24} then decreased steadily until there was no recovery of nC_{34} and greater. The addition of 1 mL of equal volumes of hexane:dichloromethane (Hex:$MeCl_2$) *at* the bottom of the evaporation tube, without using this mixture to rinse its walls, showed increased recoveries for nC_{24} and higher

(open diamonds). However, the recoveries were significantly higher when the walls were rinsed. A methanol wall rinse (open triangles) improved recovery of nC_{27} and higher, but a more dramatic improvement occurred when the walls were washed instead with equal volumes of hexane: dichloromethane (closed circles). Using this improved procedure, the recovery of the internal standard $nC_{24}D_{50}$ averaged 90%, which is consistent with the recovery of $nC_{24}H_{50}$ from the standard mix. The critical step to optimum recovery of the non-polar hydrocarbons proved to be the wall rinse with the less polar components of the solvent mixture, to reconstitute the original extraction solution.

The low recoveries of labile species nC_{12}-nC_{19} can be accounted for as irreversible evaporative loss of these species during the reduction of volume step. The increased recovery of the higher MW hydrocarbons when Hex:$MeCl_2$ was added to the reduced extract could be attributed to their higher solubility in the Hex:$MeCl_2$:MeOH mixture than in methanol alone. However, the results suggest that the wall rinse resolubilized compounds that had been deposited on the surfaces of the tubes, and rinsing with the original solvent mixture was necessary to optimize recovery. These results illustrate the need to return the extract solution to the original Hex:$MeCl_2$:MeOH solvent and wash the walls of the glassware, to re-dissolve the non-polar organics that have precipitated during the reduction of volume step.

For the higher MW n-alkanes with < 100% recoveries (> nC_{32}), lower concentrations could lead to higher recoveries because of less precipitation from the solution. To test this, recoveries were determined using the n-alkane-PAH mixture with 10 times lower concentrations than the original. The recoveries were still less than 100% for n-alkanes > nC_{32}. The results suggest that

the concentrations of the higher MW n-alkanes were low, but not enough to redissolve completely in the solvent mixture. We are finding that most of the extracts from the LaPorte, TX site have concentrations above those used in the low concentration standard mixture.

The recoveries of the PAHs also showed similar trends, based on their lability and solubility. The PAH concentrations used in the spiking mixture (and found in field samples) where lower than the n-alkanes. The lower concentrations, as well the chromatographic properties of the PAHs, led to larger error bars associated with these compounds. However, the recoveries of phenanthrene (PAH # 6) and fluoranthene (PAH # 8) were 70 and 80%, respectively, consistent with values of 70% for deuterated phenanthrene and fluoranthene previously observed using rotary evaporation after cleanup on silica (2).

Because the two classes of hydrocarbons showed similar patterns of recovery, for convenience they could be grouped for preparation of future surrogate mixtures, tailored to specific detection requirements or availability. For each group the recovery varied similarly with MW or ring size and chromatographic retention time. These groups have been identified in Table I: 1) Hydrocarbons nC_{14} - nC_{17} showed recovery similar to naphthalene - fluorene; 2) nC_{18} to phenanthrene - anthracene; 3) nC_{19} - nC_{24} to fluoranthene - pyrene; 4) nC_{24} - nC_{32}, to benz[a]anthracene – benzo[k]fluoranthene; and 5) nC_{34} - nC_{36}, to indeno[cd]pyrene – benzo[ghi]perylene.

Recovery of hydrocarbons from XAD-4 coated denuders, quartz filters and XAD-4 impregnated quartz filters.

To test recovery from the denuders, we spiked an XAD-4 coated denuder with the n-alkane-PAH mixture and extracted three times using the 'rolling rinse' method, as described earlier. The extracts were reduced in volume and each extract analyzed separately. Each extraction step removed >85% of the remaining spiked material from the denuder. Figure 4 shows the comparison of the recovery from the denuder (sum of all three extracts) with the optimized procedure for the standard compounds (above). A t-test found no difference at the 95% confidence interval between the means of recoveries. Therefore, when *compound-by compound* normalizations were made for losses during the reduction of volume procedure, the extraction efficiency of the hydrocarbons was determined to be > 95 ± 10% , overall, for the alkanes and PAHs.

Recovery of hydrocarbons from filters (quartz and XAD-4 impregnated quartz) was determined by spiking 1 mL of the n-alkane-PAH mixture to representative filters of each *t*ype. Each filter was extracted twice in Hex:$MeCl_2$:MeOH, using sonication, as described earlier. The extracts were reduced in volume and analyzed separately. Each extraction step removed >85% of the remaining spiked material from the filters. Figure 4 shows the comparison of the recovery from the filters (sum of the two extracts) with the recovery of standards. Significantly lower recoveries of the lower molecular weight n-alkanes-PAHs (< nC_{18} and associated PAHs) were observed for the spiked quartz filters, but not for the XAD-4 impregnated filters. The results for the XAD-4 impregnated filter were similar to the XAD-4 coated annular denuder, as expected for recovery from the same sorbent. When compound-by-compound normalizations were applied to account for losses during the reduction of volume, the extraction efficiency of the

hydrocarbons averaged > 95% ±10 for all standard compounds for XAD-4 impregnated quartz filters and > 95% ±10 for > nC_{18} and associated PAHs for quartz filters.

The reduced recovery from quartz filters can be attributed to evaporation of the more volatile hydrocarbons (< nC_{18} and associated PAHs) along with the solvent, from the filter surfaces before extraction. The extraction efficiency for remaining amounts of these compounds from the quartz filters was also assumed to be > 95% ±10. This assumption is supported by observation that 1) the extraction efficiency of the less volatile species on the quartz filter was > 95%, and 2) the extraction efficiency for < nC_{18} and associated PAHs from the XAD-4 impregnated quartz filters was also > 95%.

Ambient Sample

The optimized procedure was used to analyze an entire HiC IOGAPS sample that was collected during the Texas Air Quality Study – 2000 (TEXAQS-2000) at the LaPorte Airport, Houston, TX (*21*). The mean ambient temperature was ~28 °C during this period. Since the extraction efficiency was > 95% for alkanes and aromatic hydrocarbons, the reported ambient concentrations for the hydrocarbons have been corrected only for the losses during the reduction of volume procedure. Furthermore, the normalized recovery was 104% ±8 for phenanthrene-d_{10} and 97% ±6 for fluoranthene-d_{10}; anthracene-d_{10} was below the detection limit. (While the spiked amount of anthracene-d_{10} could not be quantified by GC-MS, it can be quantified using HPLC with fluorescence detection. The amount used was chosen to avoid swamping the native anthracene during HPLC analysis.)

Figure 5 shows the ambient concentrations of the n-alkanes. Most of the mass of the lighter molecular weight n-alkanes < nC_{19} was on the denuders, consistent with their higher volatility. No evidence was seen for particle loss in the first or second denuders. For n-alkanes ≥ nC_{19} a significant fraction of the mass was on the quartz filters, but even more was found on the XAD-4 impregnated after-filters. This figure illustrates the need for back-up sorbent substrates, such as the XAD-4 impregnated quartz filters, to trap SVOC desorbed from the collected particles. Figure 6 shows concentrations of the PAHs that could be detected by the GC-MS. Most of the mass of the PAHs was on the first denuder, and the concentrations generally decreased as the MW and ring size increased and the lability decreased. Naphthalene was the only PAH found in appreciable concentration on the second (downstream) denuder, and it also broke through to the XAD-4 impregnated filters. From this data, the volumetric capacity of the two denuders for naphthalene in ambient air at 28 °C was less than the 58 m^3 of air that passed through them. The apparent volumetric capacity for the other PAHs was greater than 58 m^3 but could not be established more precisely because they did not break through to the second denuder, or they were below limits of detection for the GC-MS.

Discussion

In other studies involving only one class of non-polar compounds, or classes with similar polarity and solubility, single solvents led to higher and more uniform non-normalized (uncorrected for reduction of volume losses) recovery of deuterated PAH from polyurethane foam (PUF) and filters, than we found for the solvent mixture of Hex:$MeCl_2$:MeOH. For example, Hawthorne et al. (*22*) reported non-normalized recoveries of over 95% for PAHs from

naphthalene-d_8 - benzo[ghi]perylene-d_{12} and several deuterated methoxyphenols. Fernandez et al. (*23*) reported better recoveries of naphthalene-d_8 - benzo[ghi]perylene-d_{12} extracted with hexane from PUF (82-91%), than of anthracene-d_{10} - benzo[ghi]perylene-d_{12} from filters that were extracted in a mixture of $MeCl_2$ and methanol (53-126%). Liang et al. (*24*) and Mader and Pankow (*25,26*) also found non-normalized recoveries of several deuterated PAH recoveries close to 100 % from PUF and filters that were extracted only in $MeCl_2$.

However, more comprehensive characterization of airborne semi-volatile and particulate organics frequently requires sample preparation procedures for compounds that span wide volatility, molecular weight and polarity ranges. In this paper we concentrated on the recovery of non-polar hydrocarbons from a solvent mixture that was chosen to optimize dissolution of both non-polar and polar organics, without the need for multi-step extractions. Table III summarizes our recommendations for optimal recovery of both semi-volatile and non-volatile organic compounds from air samples. The results showed how to minimize and account for losses of both semi-volatile hydrocarbons that can evaporate, and high molecular weight species that can precipitate, during concentration steps that are intended to lower limits of detection. Quantitation of polar compounds *will* require meeting these objectives with suitable laboratory and field surrogates, internal standards and detection methods, while accounting for additional causes of decreased recovery such as lower extraction efficiency and analyte degradation during sample preparation and analysis.

Our results point to the need for inclusion of a range of standards for recovery. Even for relatively inert compounds like hydrocarbons, non-normalized recovery depended on volatility,

MW, ring size and solubility. We recommend that a series of deuterated surrogates be used to account adequately for the preparation-related losses of organic species that are associated with ambient particulate matter. These surrogates should span the ranges of both volatility and polarity that are expected in an environmental matrix that could also contain multi-functional and polymeric species. Investigators should adequately describe the normalization algorithm(s) for each compound or group of compounds. A good example is provided by McDonald et al. (*27*) who used a suite of deuterated PAH from naphthalene-d_8 – coronene-d_{12}. They reported that the recovery of each analyte was normalized to the recovery of the deuterated PAH with the closest chromatographic retention time and stability.

Although we found no other reports in the literature that included non-normalized recovery data for such a wide range of alkanes and PAHs, our results for individual native compounds were similar to published recoveries of the same individual deuterated compounds added to filters and extracted with the solvents used by Mazurek et al. (*8-9*): hexane, followed by a benzene-2-propanol mixture. Additionally, the recovery data of Schauer et al. (*28-29*) for $nC_{15}D_{32}$ and $nC_{24}D_{50}$ fit nicely with the data for our optimized procedure (Figures 3 and 4). Although the Mazurek et al. (*8-9*) procedure has been widely cited, there are few reports in the literature of non-normalized recoveries of deuterated standards. The literature contains even fewer descriptions of whether and how analyte concentrations were corrected for variation of losses with MW or ring size.

Our results have several implications for ongoing efforts to characterize airborne PM and associated semi-volatile compounds. First, caution must be applied to *generalizing* the

recoveries of SVOC from clean filters in the laboratory. The evaporation of labile species from filters may not represent the true behavior of the SVOC in PM because of their stronger adsorption to PM than to the filter substrates. Overestimates of their ambient PM-associated concentrations would result. Second, caution must also be applied when interpreting results based on one surrogate for recovery of many compounds. Basing ambient concentrations on recovery of a mid-range (volatility and MW) surrogate would lead to worsening underestimation of ambient concentrations of compounds the more different in volatility and MW they were from the surrogate. Problems could arise concerning mass closure estimates from such studies and they should be interpreted with caution. This may have been the case for the extensive characterization of PM sources by Rogge et al. (*10-17*) who used only $nC_{24}D_{50}$ for recovery of all non-derivatized compounds. Our results suggest that using only $nC_{24}D_{50}$ could underestimate PM concentrations for both lighter and heavier hydrocarbons outside the nC_{19} - nC_{34} range. Similarly, Fraser et al. (*30, 31*) used $nC_{24}D_{50}$ as the recovery surrogate for PM, but also added to a PUF, without clearly detailing the normalization algorithm for the semi-volatile compounds. There is good agreement with our data for these compounds. However, significant bias could exist even when a few surrogates for recovery are used, unless recovery has been measured and normalized through a series of related compounds. In spite of improved procedures that use solvent mixtures (or sequential solvent extraction) and two deuterated species ($nC_{15}D_{32}$ and $nC_{24}D_{50}$) for recovery of non-polar compounds, concerns may remain about interpretation of these recent studies (*28, 29, 31-34*). We found two and a half times lower recovery for $nC_{15}H_{32}$ than for n $C_{24}H_{50}$. Quantitative comparisons among the results of many investigators will be affected by unclear explanation of normalized algorithm and inconsistent use of surrogates.

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Disclaimer

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References

1. Gundel L.A.; Lane, D.A. In Gas and Particle Phase Measurements of Atmospheric Organic Compounds, Lane, D.A., Ed. in Vol. 2, *Advances in Environmental, Industrial and Process Control Technologies,* Gordon and Breach: Newark, **1999,** 287-332.
2. Gundel, L.A.; Lee, V.C.; Mahanama, K.R.R.; Stevens, R.K.; Daisey, J.M. *Atmos. Environ.,* **1995,** *29,* 1719.
3. Grosjean, D. *Anal. Chem.,* **1975,** *47,* 797.
4. Appel, B.R.; Hoffer, E.M.; Kothny, E.L.; Wall, S.M.; Haik, M.; Knights R.L. *Environ. Sci. Technol.*, **1979,** *13*, 98.
5. Cadle, S.H.; Groblicki, P.J. In *Particulate Carbon: Atmospheric Life Cycle*, Wolff G.T.; Klimisch, R.L., Eds., Plenum Press: New York, **1982,** 89.
6. Daisey, J.M.; Kneip, T. J.; Hawryluk, I.; Mukai, F. *Environ. Sci. Technol.*, **1980,** *14* (12), 1487.
7. Gundel, L.A.; Daisey J.M.; de Carvalho, L.R.F.; Kado, N.Y.; Schuetzle, D. *Environ. Sci. Technol.,* **1993,** *10*, 2112.
8. Mazurek, M.A.; Simoneit, B.R.T.; Cass, G.R.; Gray, H.A. *Int. J. Environ. Anal. Chem.*, **1987,** *29,* 119.
9. Mazurek, M.A.; Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.* **1991,** *25,* 684.
10. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Gass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1991,** *25,* 1112.
11. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Gass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1993**, *27,* 636.
12. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Gass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1993**, *27,* 1892.
13. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Gass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1993**, *27,* 2700.
14. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Gass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1993**, *27,* 2736.
15. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Gass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1994**, *28*, 1375.
16. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Gass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1997**, *31*, 2726.
17. Rogge, W.F.; Hildemann, L.M.; Mazurek, M.A.; Gass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1997**, *31*, 2731.
18. Gundel L.A. Standard operating procedures for coating annular denuders with XAD-4 resin; US EPA Chemical Speciation Program, **1998,** PUB-3143.
19. Gundel, L.A.; Daisey, J.M. and Stevens, R.K. Quantitative Organic Vapor-Particle Sampler, **1998** US Patent 5,763,360.
20. Gundel, L.A.; Daisey, J.M. and Stevens, R.K. Method for fabricating a quantitative integrated diffusion vapor-particle sampler for sampling, detection and quantitation of semi-volatile organic gases, vapors and particulate components, **2001**, US Patent 6,226,852.
21. Swartz E.; Stockburger, L.; Michel, C.; Lane, D.A.; Pang, Y.; Gundel, L.A. Characterization of Ambient Aerosols at LaPorte, Texas, during TEXAQS-2000, presented at the 20th Annual Conference of the American Association for Aerosol Research, Portland, OR, Oct 15-19, 2001.

22. Hawthorne, Miller, D.J.; Langenfeld, J.J.; Krieger, M.S. *Environ. Sci. Technol.*, **1992**, *26,* 2251-2262.
23. Fernandez, P.; Grimalt, J.O.; Vilanova, R.M. *Environ. Sci. Technol.*, **2002**, *36,* 1162-1168.
24. Liang, C; Pankow, J.F.; Odum, J.R.; Seinfeld, J.H. *Environ. Sci. Technol.*, **1997**, *31,* 3086-3092.
25. Mader, B.T.; Pankow J.F.;*Atmos. Environ.*, **2000**, *34*, 4879-4887.
26. Mader, B.T.; Pankow J.F.; *Atmos. Environ.*, **2001**, *35*, 1217-1223.
27. McDonald, J.D.; Zielinska, B.; Fujita, E.M.; Sagebiiel, J.C.; Chow, J.C.; Watson, J.G. *Environ. Sci. Technol.*, **2000**, *34,* 2080-2091.
28. Schauer J.J.; Kleeman, M.J., Cass, G.R.; Simoneit, B.R.T; *Environ. Sci. Technol.*, **1999**, *33,* 1566-1577.
29. Schauer J.J.; Kleeman, M.J., Cass, G.R.; Simoneit, B.R.T; *Environ. Sci. Technol.*, **2002**, *36,* 567-575.
30. Fraser, M.P; Cass, G.R.; Simoneit, B.R.T; Rasmussen, R.A. *Environ. Sci. Technol.*, **1997**, *31,* 2356-2367.
31. Fraser, M.P; Cass, G.R.; Simoneit, B.R.T; Rasmussen, R.A. *Environ. Sci. Technol.*, **1998**, *32,* 1760-1770.
32. Schauer J.J.; Kleeman, M.J., Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **2002**, *36,* 1169-1180.
33. Schauer J.J.; Kleeman, M.J., Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **2001**, *35,* 1716-1728.
34. Schauer J.J.; Kleeman, M.J., Cass, G.R.; Simoneit, B.R.T. *Environ. Sci. Technol.*, **1999**, *33,* 1778-1587.

Table I. n-Alkane-PAH spiking mixture.

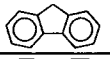
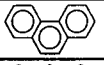
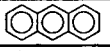
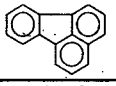
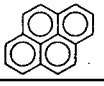
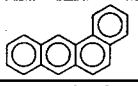
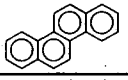
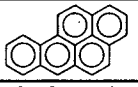
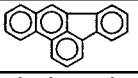
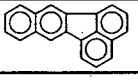
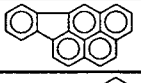
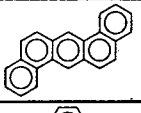
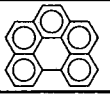
Group	Alkanes	Carbon #	µg/mL	PAHs	Structure	PAH #	µg/mL
-	nC_{12}	12	5.7				
-	nC_{13}	13	7.6				
I	nC_{14}	14	5.9	Naphthalene		1	1.0
I	nC_{15}	15	11.8	2-methyl naphthalene		2	1.0
I	nC_{16}	16	6.0	Acenaphthylene		3	1.0
I	nC_{17}	17	5.5	Acenaphthene		4	1.0
I				Fluorene		5	1.0
II	nC_{18}	18	10.4	Phenanthrene		6	1.0
II				Anthracene		7	1.0
III	nC_{19}	19	8.4	Fluoranthene		8	1.0
III	nC_{20}	20	7.4	Pyrene		9	1.0
III	nC_{21}	21	7.3				
III	nC_{22}	22	7.1				
III	nC_{23}	23	6.6				
III	nC_{24}	24	8.0				
IV	nC_{25}	25	6.9	Benzo[a]anthracene		10	1.0
IV	nC_{26}	26	6.8	Chrysene		11	1.0
IV	nC_{27}	27	6.9	Benzo[a]pyrene		12	1.0
IV	nC_{28}	28	7.7	Benzo[b]fluoranthene		13	1.0
IV	nC_{29}	29	6.7	Benzo[k]fluoranthene		14	1.0
IV	nC_{30}	30	8.8				
IV	nC_{32}	32	7.4				
V	nC_{34}	34	6.3	Indeno[1,2,3-cd]pyrene		15	1.0
V	nC_{36}	36	7.3	Dibenzo[a,h]anthracene		16	1.0
V				Benzo[ghi]perylene		17	1.0
-	nC_{38}	38	10.0				
-	nC_{40}	40	7.6				

Table II. Program for reduction of volume with Labconco RapidVap® Vacuum Evaporating System.

Temp (°C)	Pressure (mbar)	Vortex Speed	Time (min)	Comment
35	-	-	-	Preheat system
35	750	28%	5	Prevent bumping and evaporate dichloromethane
35	650	28%	5	Prevent bumping and evaporate dichloromethane
40	550	28%	15	Evaporate hexane
45	400	30%	20	Evaporate hexane and methanol
50	250	34%	as needed	Reduce to final volume of 0.5 mL (methanol)

Table III. Recommendations for optimal recovery of airborne semivolatile and particulate organic compounds from sorbent and filter media

Issue	Action	Concerns
Collection media	• Choose high-capacity extractable sorbent for gas phase; • Inert extractable filter or surface for particles	• Few options
Solvents	• Choose efficient solvent mixture	• Polarity • reactivity, • solubility, • MW
Concentration	• Optimize with complete range of target analytes; • Choose several surrogates for range of functional groups, volatility, solubility and molecular weight; • Re-solubilize analytes by reconstituting extract in original (or improved) solvent mixture, including wall rinse; • Choose appropriate internal standards for detection technique; • Validate with standard mixture, blanks and SRM before sample preparation; • Track and report recovery data.	• Irreversible volatility losses; • Precipitation as solvent composition changes
Extraction	lidate before routine sample preparation	
Gaseous SVOC	• Validate by adding standards and surrogates to clean sorbent media, analyze; • Add recovery surrogates to collection media	• Standards on sorbent may not be representative of behavior during sampling
Particles	• Add standards and surrogates to clean filter and sorbent impregnated filters, analyze; • Extract, concentrate, analyze; • Validate with particulate SRMs when available; • Add recovery surrogates to sample filters immediately before extraction, without drying	• Dry, particle-free quartz filter has limited capacity for SVOC
Detection	• Choose best analytical method(s); • Determine response factors with authentic standards	

Quantitation	• Choose appropriate surrogate for extract volume change • Add internal standard(s) for instrument response	
Data reduction	• Track and report surrogate recovery data • Report target analyte concentrations per unit air volume at ambient T, P • Report measurement uncertainties • Document procedures	• Confusion about standard conditions; • Inadequate QA/QC
Storage	• Monitor sample extracts periodically for losses	

Figure Captions

Figure 1. Schematic of the High Capacity Integrated Organic Gas and Particle Sampler (HiC IOGAPS).

Figure 2. Flow diagram of sample preparation for the HiC IOGAPS.

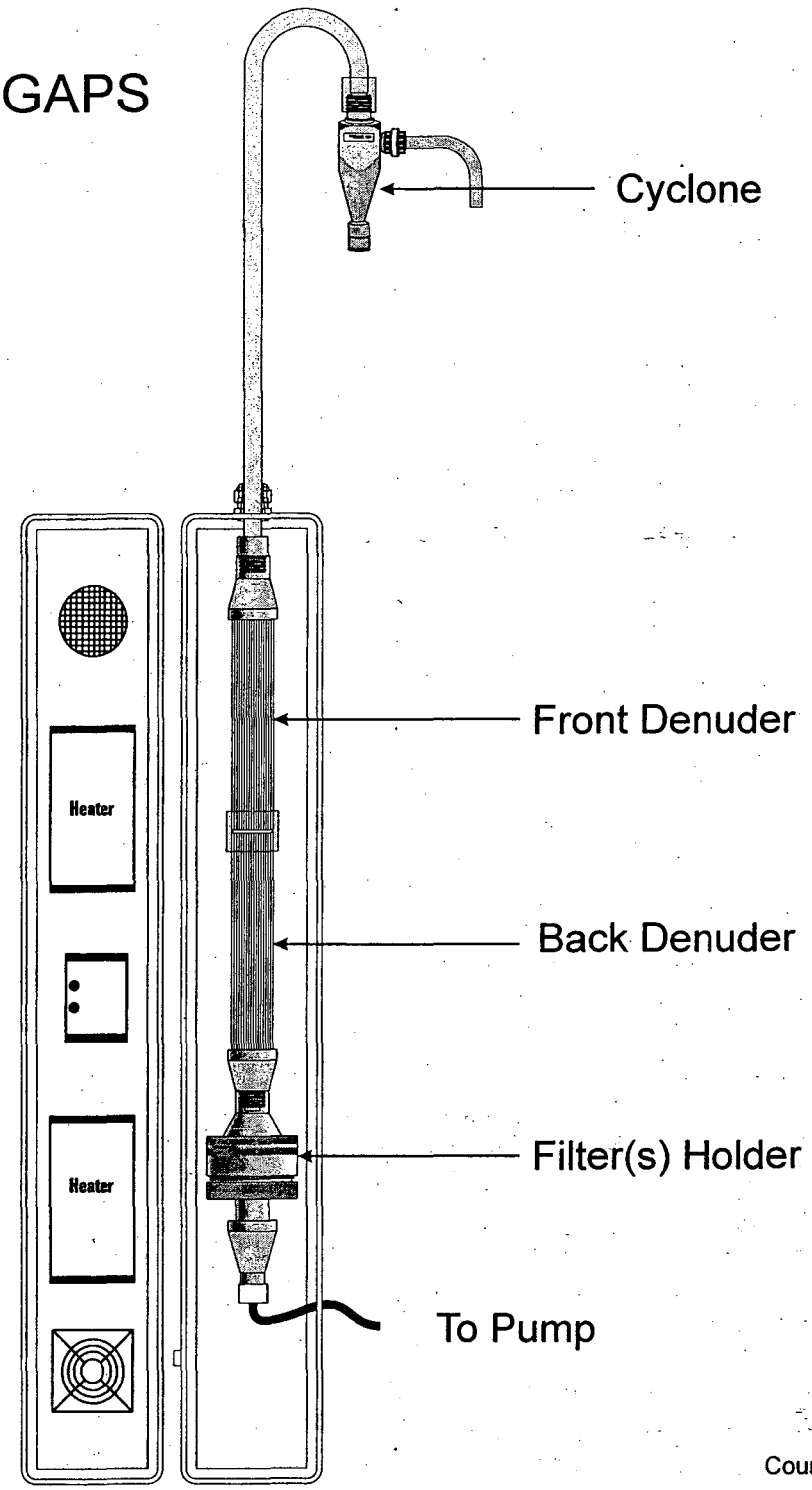
Figure 3. Percent recovery of n-alkanes (a) and PAHs (b) from various reduction of volume procedures. A reduced extract only (0.5 mL) is shown as open squares; the same 0.5 mL reduced extract with addition of 1 mL of Hex:$MeCl_2$ is shown as open diamonds; a reduced extract with the Labconco glassware rinsed with 1 mL MeOH is shown as open triangles; a reduced extract with the Labaconco glassware rinsed with 1 mL of Hex:$MeCl_2$ are shown as closed circles. The open circle markers (at carbon # 24.5) show the recovery of the laboratory surrogate $nC_{24}D_{50}$. The error bars represent the uncertainty at the 1σ level.

Figure 4. Comparison of the percent recovery of n-alkanes(a) and PAHs(b) from the reduction of volume procedure, the extraction of an 8-channel XAD-4 denuder, the extraction of a quartz filter and the extraction of a XAD-4 impregnated quartz filter. The open markers are the recovery of the internal standard $nC_{24}D_{50}$. The error bars represent the uncertainty at the 1σ level.

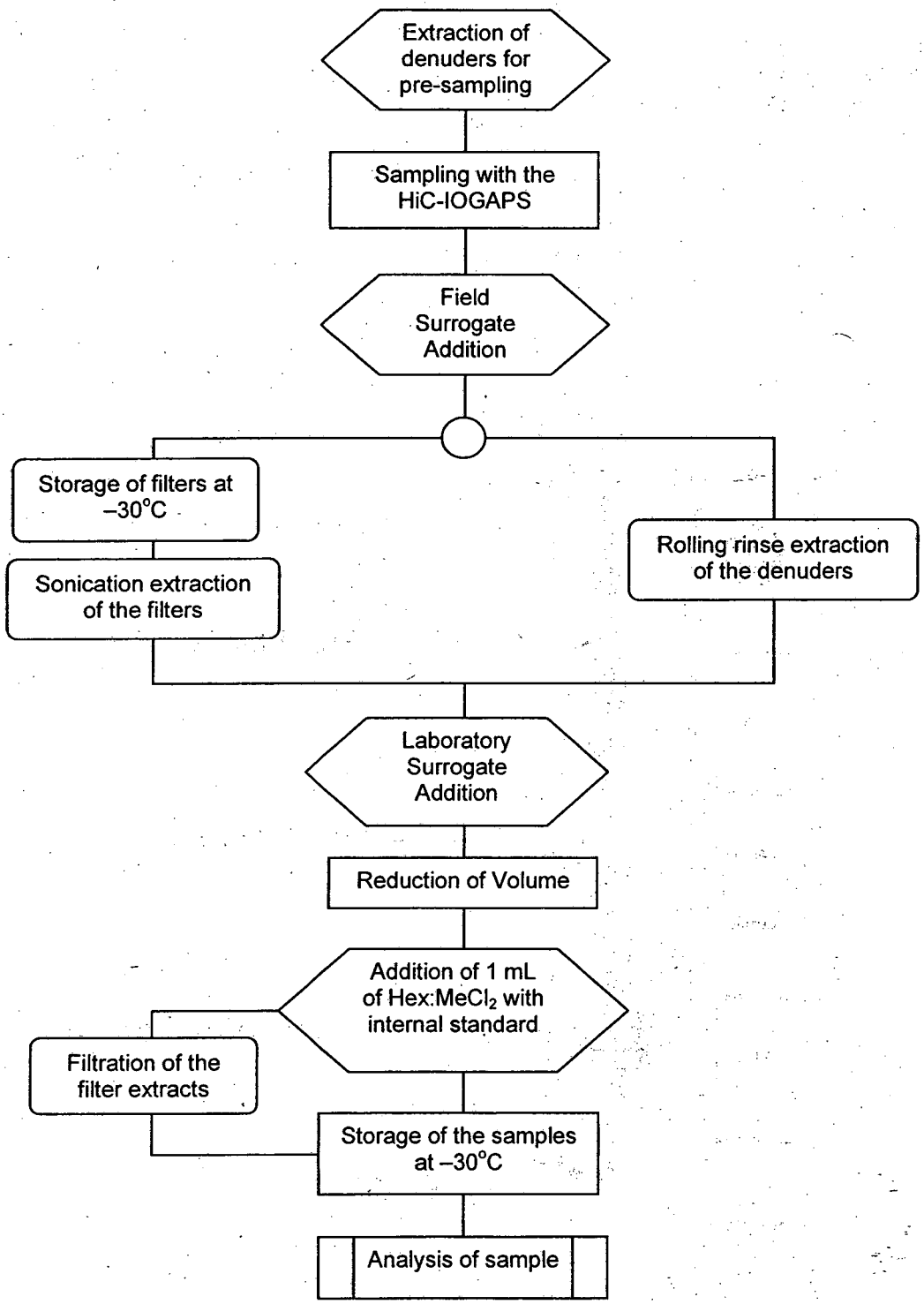
Figure 5. Average concentration of n-alkanes for LaPorte, TX on 8/31/2000 from 00:00-11:30 (Local Time), including the contribution from each HiC IOGAPS component. The error bars represent the uncertainty at the 1σ level.

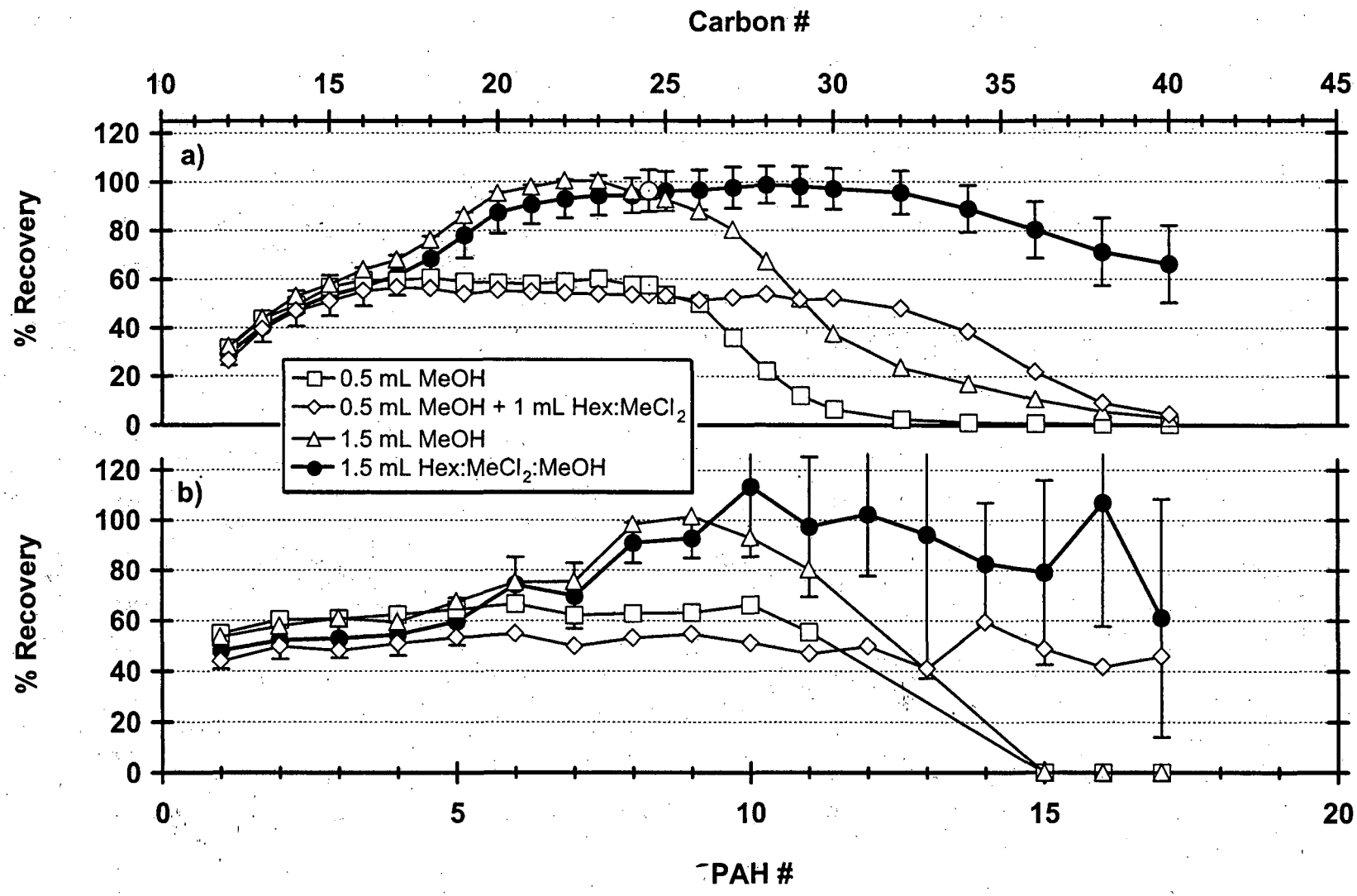
Figure 6. Average concentration of PAHs for LaPorte, TX on 8/31/2000 from 00:10-11:30 (Local Time) including the contribution from each HiC IOGAPS component. The error bars represent the uncertainty at the 1σ level.

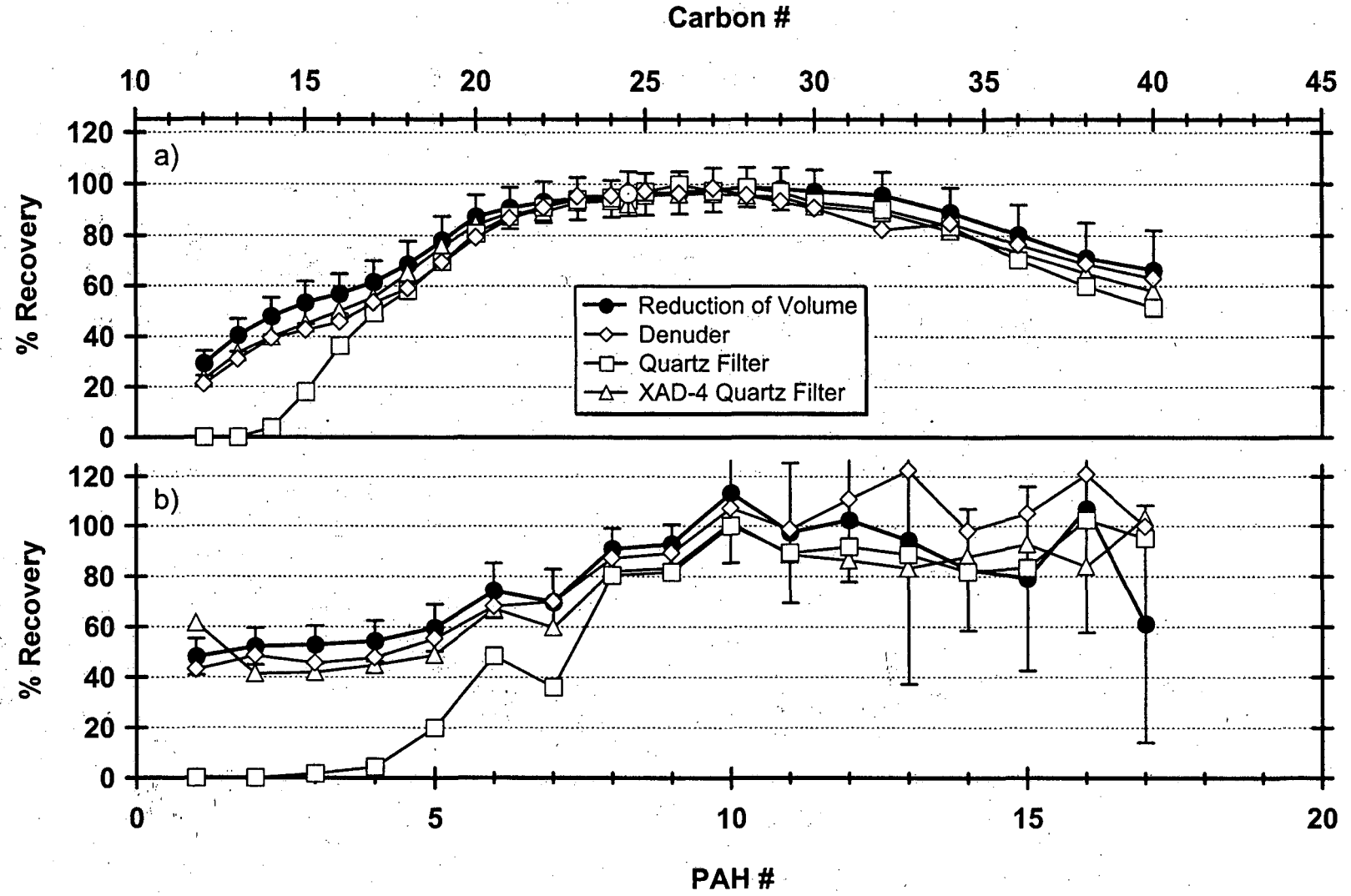
HiC IOGAPS

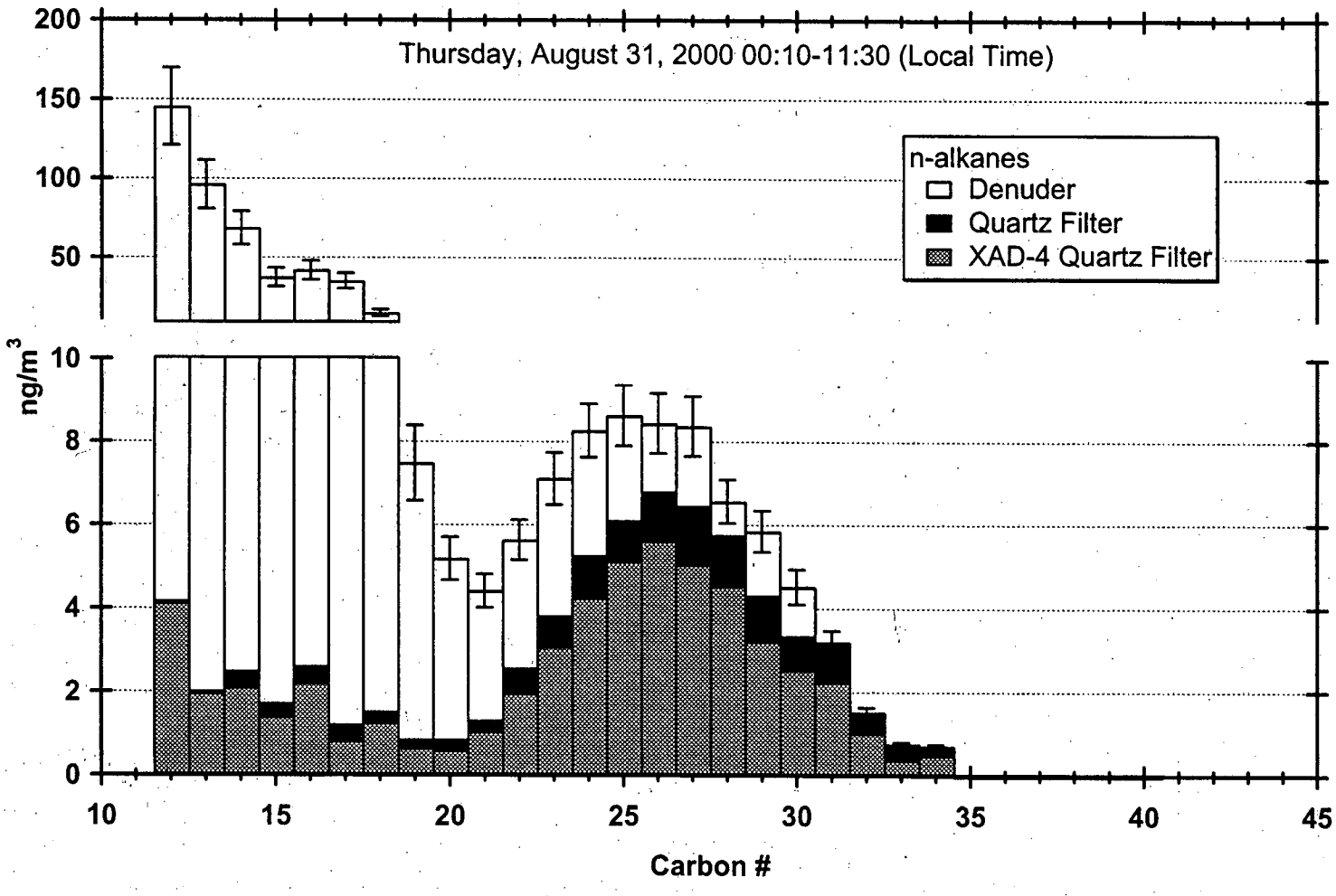


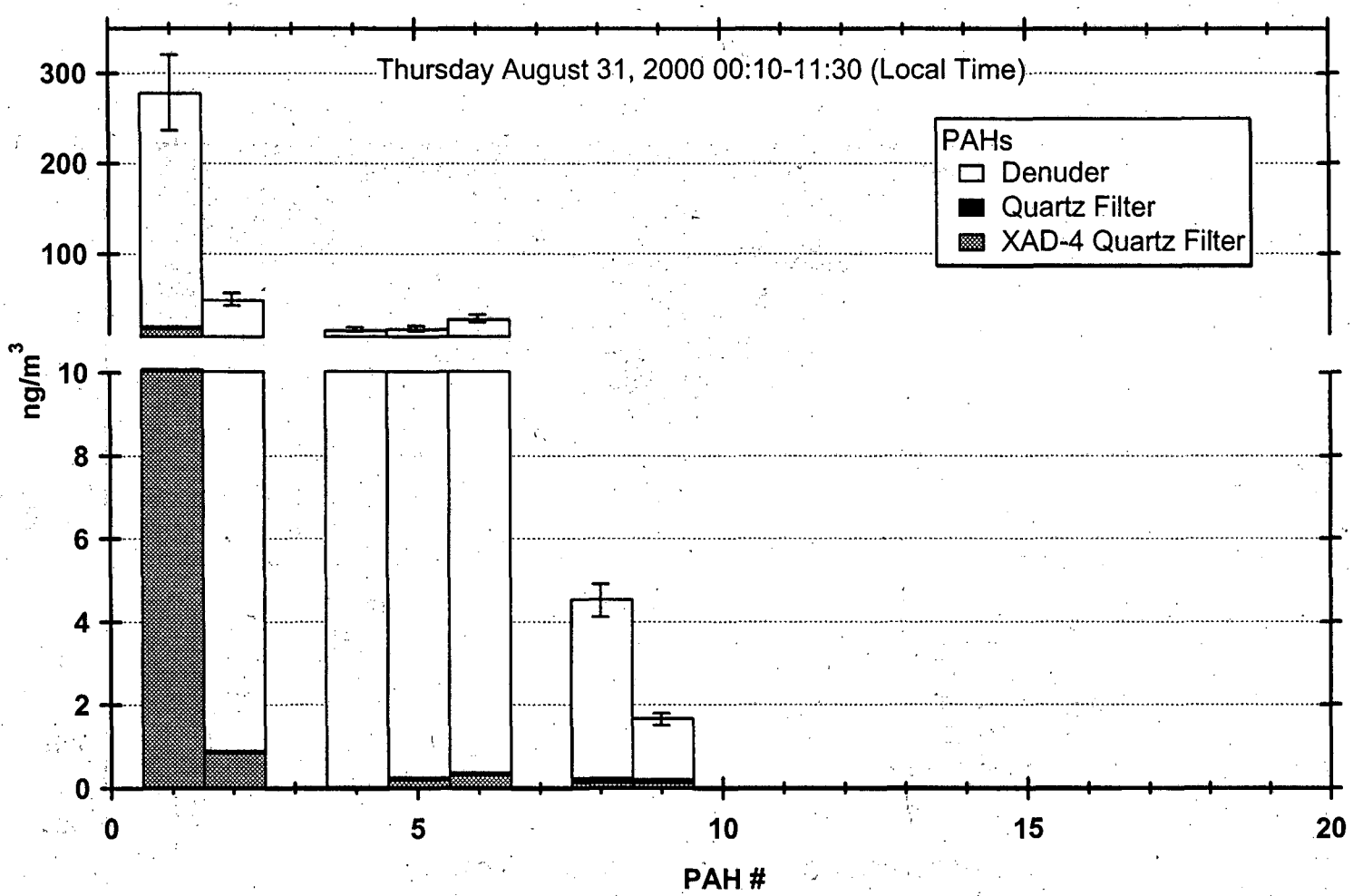
Courtesy of URG


Extraction of denuders for pre-sampling
Sampling with the HiC-IOGAPS
Field Surrogate Addition
Storage of filters at –30°C
Sonication extraction of the filters
Rolling rinse extraction of the denuders
Laboratory Surrogate Addition
Reduction of Volume
Addition of 1 mL of Hex:$MeCl_2$ with internal standard
Filtration of the filter extracts
Storage of the samples at –30°C
Analysis of sample


Carbon #
10
15
20
25
30
35
40
45
a)
b)
% Recovery
% Recovery
120
100
80
60
40
20
0
0.5 mL MeOH
0.5 mL MeOH + 1 mL Hex:MeCl2
1.5 mL MeOH
1.5 mL Hex:MeCl2:MeOH
0
5
10
15
20
PAH #


Carbon #
10
15
20
25
30
35
40
45
a)
b)
% Recovery
% Recovery
120
100
80
60
40
20
0
Reduction of Volume
Denuder
Quartz Filter
XAD-4 Quartz Filter
0
5
10
15
20
PAH #


Thursday, August 31, 2000 00:10-11:30 (Local Time)
n-alkanes
Denuder
Quartz Filter
XAD-4 Quartz Filter
ng/m3
Carbon #
200
150
100
50
10
8
6
4
2
0
10
15
20
25
30
35
40
45


Thursday August 31, 2000 00:10-11:30 (Local Time)
PAHs
Denuder
Quartz Filter
XAD-4 Quartz Filter
ng/m3
300
200
100
10
8
6
4
2
0
0
5
10
15
20
PAH #

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