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Department of Chemistry
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**Approved for Distribution:**

**Robert B. Gagosian, Chairman**
**Department of Chemistry**

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## LIST OF ABBREVIATIONS

CDS - Chromatography Data System
CPI - carbon preference index
DC - derivatized compound
EEOM - ether extractable organic matter
FAME - fatty acid methyl ester
f.s. - full scale
GC - gas chromatography
GC/MS combined gas chromatography-mass spectrometry
GFF - glass fiber filter
HRGC - high resolution glass capillary gas chromatography
HRGC/MS combined high resolution glass capillary gas chromatography-mass spectrometry
ICS - impactor collection substrate
ID - inner diameter
IDL - instrument detection limit
LOD - limit of detection
LOQ - limit of quantitation
LP - Lab Procedure
MW(DC) molecular weight of the derivatized compound
MW(UC) molecular weight of the underivatized compound
NBS - National Bureau of Standards
OD - outer diameter
PAH - polycyclic aromatic hydrocarbon
PD-$H_2O$ - permanganate distilled water
PS - pear-shaped
PUF - polyurethane foam
QS - quantitation standard
RB - round bottom
RRF - relative response factor
RS - recovery standard
SC - screw-cap
SEAREX Sea-Air Exchange program
SRM - Standard Reference Material
SS - stainless steel
TM - registered trademark or brand name
TOC - total organic carbon
UC - underivatized compound
UCM - unresolved complex mixture
WHOI - Woods Hole Oceanographic Institution
X - analyte

ABSTRACT

A procedure is described for the collection of remote marine aerosol samples by high-volume filtration, cascade impaction, dry fallout collection and rain. Samples were analyzed quantitatively for five classes of naturally occurring lipids (n-alkanes, wax esters, fatty alcohols, sterols, and fatty acids) and polycyclic aromatic hydrocarbons (PAHs). Air samples (4,000-10,000 $m^3$) were collected on glass fiber filters under automatic control. Rain samples of 1-5 L were collected on an event basis. Filters and rain samples were extracted with methylene chloride. The extracts were fractionated into discrete chemical classes by silica-gel adsorption chromatography. The fractions were derivatized if necessary and analyzed by HRGC and HRGC/MS. A second filter extraction was required for fatty acid salt analysis. Internal standards were used to quantify recoveries and concentrations. Mean recoveries relative to the internal standards were 96.5 $\pm$ 2.8% for $C_{18}$-$C_{36}$ n-alkanes, 96.4 $\pm$ 5.3% for $C_{20}$-$C_{30}$ n-fatty acids, 92.5 $\pm$ 4.5% for $C_{14}$-$C_{30}$ n-fatty alcohols and 93.3 $\pm$ 1.4% for cholesterol. Typical blanks and concentrations for remote marine aerosol and rain samples are described and compared with other methods used in coastal marine, rural and suburban sampling locations.

ACKNOWLEDGEMENTS

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# I. INTRODUCTION

Questions about the origin of the blue haze over forested areas [Went, 1960; Rasmussen and Went, 1965; Stevens et al., 1980], the effects that trace levels of organic compounds have on the origin and stability of fogs [Barger and Garrett, 1970; Barger and Garrett, 1976; Graedel and Weschler, 1981; Gill et al., 1983], efforts to measure the atmospheric contribution of petroleum hydrocarbon pollution of the world's ocean [Garrett and Smagin, 1976], and speculations on the budget of non-methane organic carbon in the global troposphere [Duce, 1978] have led many investigators into areas remote from man's activities to look at the organic compound composition of the atmosphere. Characterization of trace amounts of organic compounds in "clean air" is a problem distinctly different from the monitoring of organic pollutants in urban, suburban or rural continental areas. Typically, aliphatic and aromatic hydrocarbons derived from petroleum and fossil fuel combustion are measured in analyses of atmospheric samples from urban and suburban areas [Lamb et al., 1980]. On the other hand, biogenic lipids, in a variety of compound classes, may predominate in background aerosol samples from rural continental, seashore and coastal marine locations [Simoneit, 1980; Simoneit and Mazurek, 1982]. It is the wide variety of compound classes contained in these lipid materials, and their orders of magnitude lower concentrations at remote marine locations which presents unique analytical problems.

Thus far, ten different classes of organic compounds have been detected in aerosol samples from rural continental, seashore and marine sites. These so-called "background aerosols" were collected under clean air conditions away from local sources of contamination and anthropogenic emissions. Normal alkanes are most commonly analyzed [Quinn and Wade, 1972; Ketseridis et al., 1976; Cautreels and van Cauwenberghe, 1977; Simoneit, 1977, 1979; Eichmann et al., 1979, 1980; Marty et al., 1979; Van Vaeck et al., 1979; Broddin et al., 1980; Gagosian et al., 1981, 1982; Cox et al., 1982; Doskey, 1982; Marty and Saliot, 1982; Simoneit and Mazurek, 1982; Schneider et al., 1983], but isoprenoid hydrocarbons [Rasmussen and Went, 1965; Simoneit, 1980; Simoneit and Mazurek, 1982]

and a complex mixture of unresolved aliphatic petroleum hydrocarbons are also found [Ketseridis et al., 1976; Marty et al., 1979; Broddin et al., 1980; Simoneit, 1980; Cox et al., 1982; Simoneit and Mazurek, 1982]. Other naturally derived lipid-type compound classes found in background aerosols are: fatty acids [Barger and Garrett, 1970, 1976; Quinn and Wade, 1972; Ketseridis et al., 1976; Cautreels and van Cauwenberghe, 1977; Simoneit, 1977, 1979, 1980; Eichmann et al., 1979, 1980; Marty et al., 1979; Van Vaeck et al., 1979; Gagosian et al., 1981, 1982; Cox et al., 1982; Simoneit and Mazurek, 1982], terpenoid acids [Simoneit, 1980; Simoneit and Mazurek, 1982], fatty alcohols [Simoneit, 1977, 1979, 1980; Barbier et al., 1981; Gagosian et al., 1981, 1982; Simoneit and Mazurek, 1982] and sterols [Barbier et al., 1981; Gagosian et al., 1981, 1982]. Some methods [Ketseridis et al., 1976; Cautreels and van Cauwenberghe, 1977; Van Vaeck et al., 1979; Broddin et al., 1980; Giam et al., 1980; Atlas and Giam, 1981] also included analyses of anthropogenic compounds such as PAHs and phthalate esters.

Sampling of atmospheric particulate matter for organic compound analysis has been done primarily through the use of hi-vol air samplers with glass fiber filters. Simoneit [1977, 1979] has also used nylon nets to sample large (> 2 μm) particles in the eastern tropical Atlantic near the coast of Africa. Recently, size-fractionated aerosol samples have been collected [Hoffman and Duce, 1977; Van Vaeck et al., 1979; Broddin et al., 1980; Chesselet et al., 1981; Marty and Saliot, 1982; Schneider et al., 1983; Schneider and Gagosian, 1984] in order to determine the particle size distribution of the organic compounds and whether they were associated with the large sea-salt particles (marine source), or with the smaller ($r \leq 0.25$ μm) continentally derived particles. The concentration of particulate organic matter may also be affected by interactions with gas/vapor phase organic compounds. This may be especially true for aliphatic and aromatic hydrocarbons. Hahn [1980] has reviewed much of the work in this respect, with special emphasis on the gas and aerosol distribution of the n-alkanes.

We report here a description of the sampling equipment, sampling protocols, sample extraction, fractionation and derivatization procedures,

and high resolution glass capillary gas chromatography used for the analysis of five naturally occurring lipid compound classes and PAHs in background aerosol and rain samples collected at a remote marine location (Enewetak atoll) as part of the SEA-AIR EXCHANGE program (SEAREX) [Duce, 1981]. Results from recovery experiments and analysis of aerosol samples collected at Pigeon Key, Florida and Enewetak atoll, Marshall Islands are provided to critically evaluate the technique and demonstrate its applicability to background level samples in remote marine locations.

## II. EXPERIMENTAL

Automatic control of atmospheric sampling: The collection system was controlled automatically according to real-time meteorological parameters to sample only when "clean air" conditions prevailed; and therefore, only the uncontaminated background aerosol was collected [Duce, 1981]. Relevant meteorological and chemical conditions were monitored continuously: wind speed, direction, condensation nuclei counts, precipitation, ozone and radon. Collection was stopped immediately whenever the surface wind direction was not from the open sea, when the wind speed dropped below 5 knots, when the condensation nuclei count exceeded 750 particles/$cm^3$, when precipitation started or when either ozone or radon concentrations were outside the pre-determined ranges for each site. Sampling began again only when all minimum conditions were met.

Hi-vol air sampler: A schematic diagram of our high-volume atmospheric sampler (hi-vol air sampler) is shown in Figure 1. The glass fiber filter (GFF) for collecting aerosol samples is mounted inside an all-metal frame (Figure 2). Top and bottom pieces are aluminum and the bottom piece is recessed to hold a perforated sheet of stainless steel to support the glass fiber filter. The GFF frame is mounted on top of a General Metal Works 8" x 10" filter holder. The filter holder has been modified with two additional threaded studs (one each in the middle of the long sides) to prevent bending of the filter frame and leakage of air. A 1/8" thick, 50 durometer silicone rubber gasket (Chase-Walton,

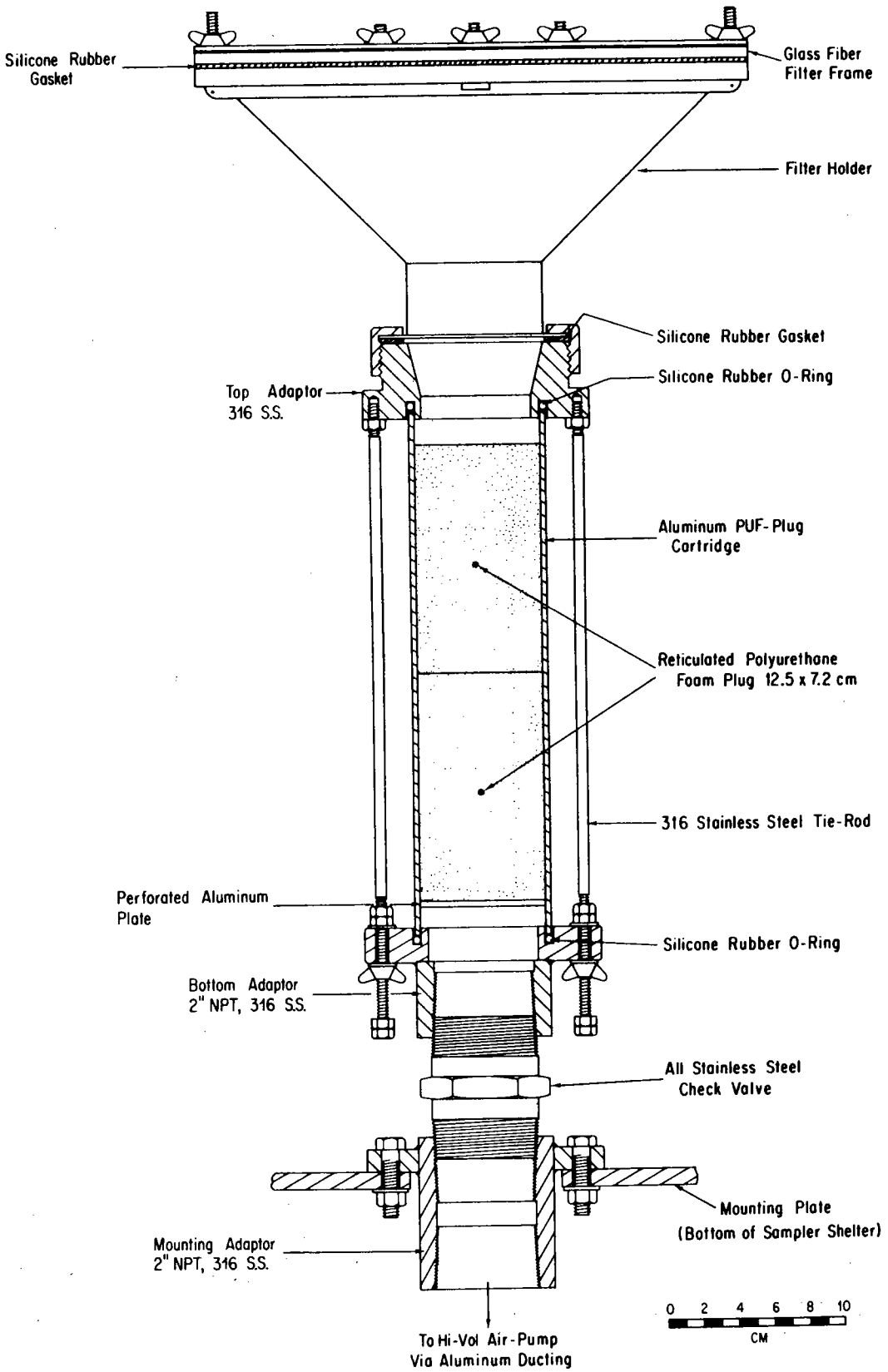


Figure 1 Hi-vol air sampler

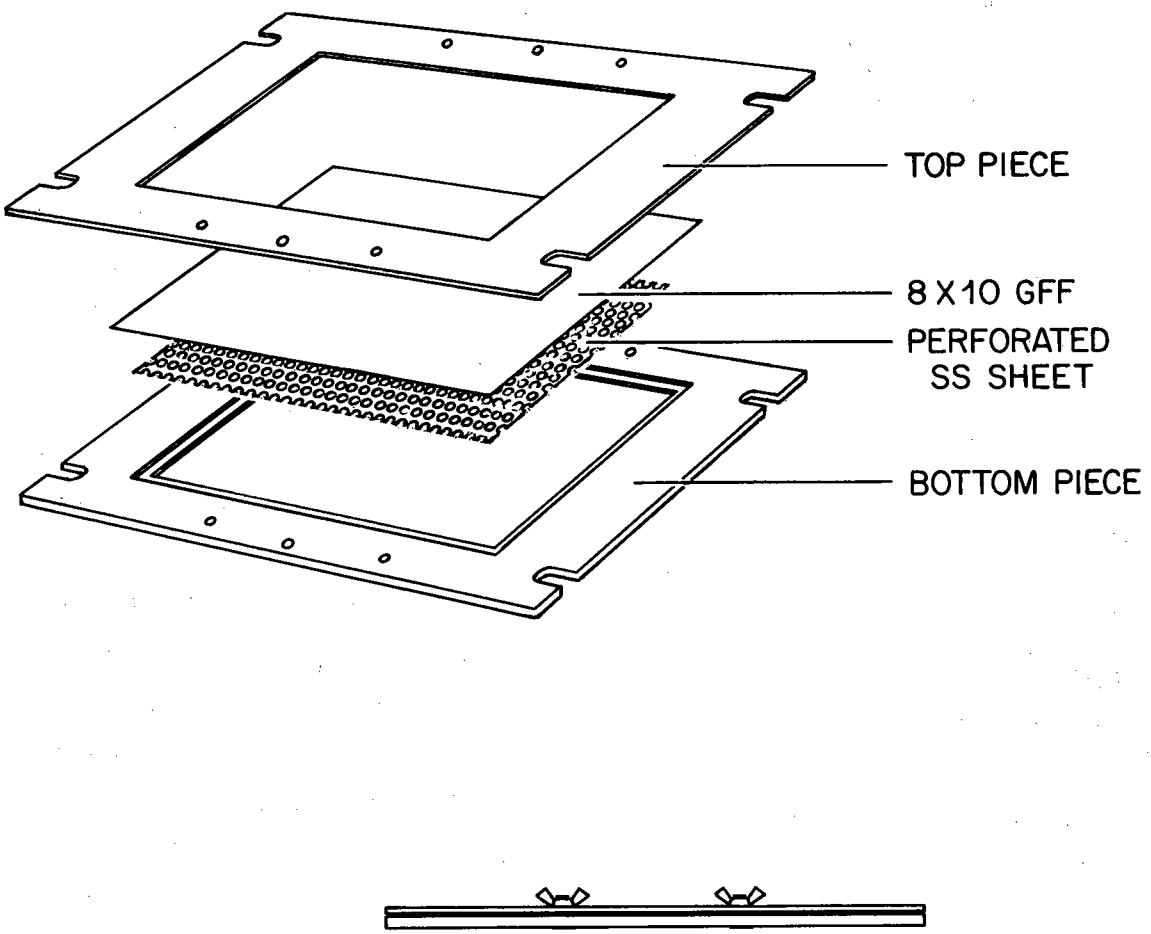


Figure 2 Glass fiber filter frame. (Top) Exploded-view of GFF frame showing placement of GFF and performated SS support. (Bottom) Side view of filter frame assembled and secured with wing-nuts.

Hudson, MA) is used between the GFF frame and filter holder to prevent leakage of air as well. Top, bottom and mounting adaptors were custom-machined from 316 SS stock (Aurele's machine shop, New Bedford, MA). The aluminum PUF-plug cartridge (290 mm x 76 mm OD, 3 mm wall) is held in place between the top and bottom adaptors with 3 stainless steel tie-rods against silicone rubber O-rings for an air-tight/leak-free connection. The check-valve (Check-all valve, Model No. CON-200-SS, Flow Controls, Inc., Needham, MA) has a stainless steel body and spring with a silicone rubber O-ring seal. Threads were sealed with teflon tape. This valve prevented back diffusion of material from the pump and ducting to the sampler during non-pumping intervals. The spring pressure (~ 1/8" psi cracking pressure) was sufficient to close the valve firmly, before the pump stopped, thus assuring little chance of contamination. Two complete assemblies were mounted in individual, all metal shelters (aluminum and 316 SS; see Figure 3) outside the windward railing on the top level platform of a 20 m aluminum tower [Duce, 1981]. All components of the air sampler were degreased, washed with 3 percent Micro$^{TM}$ in water, rinsed with distilled water, acetone and methylene chloride prior to assembly. The sample shelter and the aluminum ducting were rinsed on the tower with distilled water, acetone and methylene chloride after assembly. At Enewetak, each air sampler was connected to a Clements Cadillac Model HP33 blower-suction unit through 20 m of flexible aluminum ducting (bendway duct, 3" ID, Greene Rubber Co., Cambridge, MA; see Figure 4). Sections of tubing were joined together with 3" OD connectors and hose clamps (316 SS, L. S. Chase and Sons., Fall River, MA) and sealed by wrapping the seam with teflon tape. Prior to sampling, the ducting was checked for leaks under maximum vacuum by plugging the air sampler with a cartridge containing a solid aluminum plate or other suitable device and running the air pump at ~ 120% of rated voltage. The system was considered leak free when no back-pressure or negative back-pressure was measured at the pump outlet using the "A" orifice (see below).

The flexible aluminum ducting proved to be fairly fragile: holes formed where the wind caused it to rub against the tower, and sea-salt pitting occurred after 1-2 months of exposure. Daily inspection for

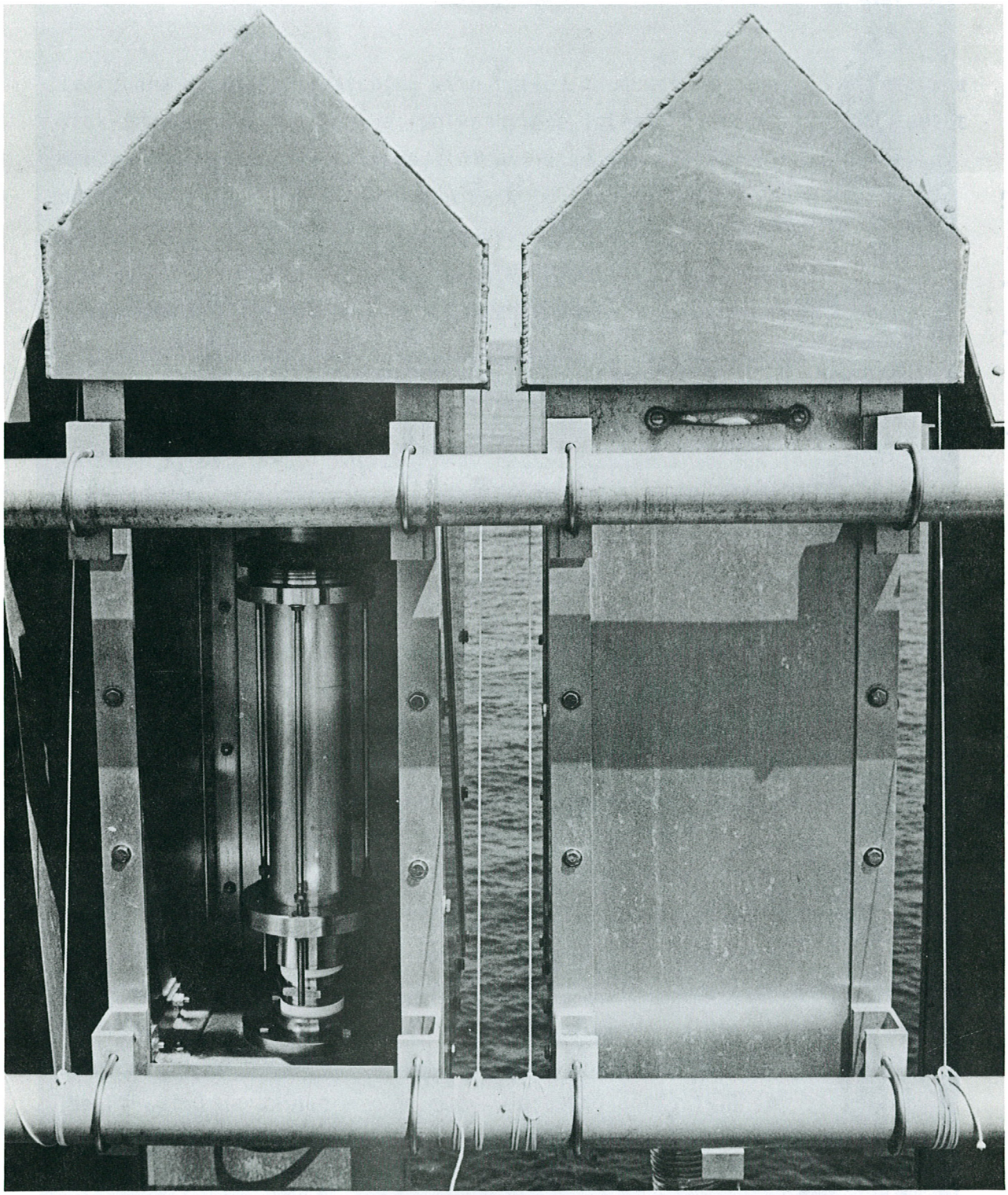

Figure 3 Photograph of hi-vol sampler shelters. Shelters are mounted on the platform railings at the top of the air sampling tower. Door on left shelter is open to show placement of hi-vol air sampler. Door on right is closed to show normal sampling position.

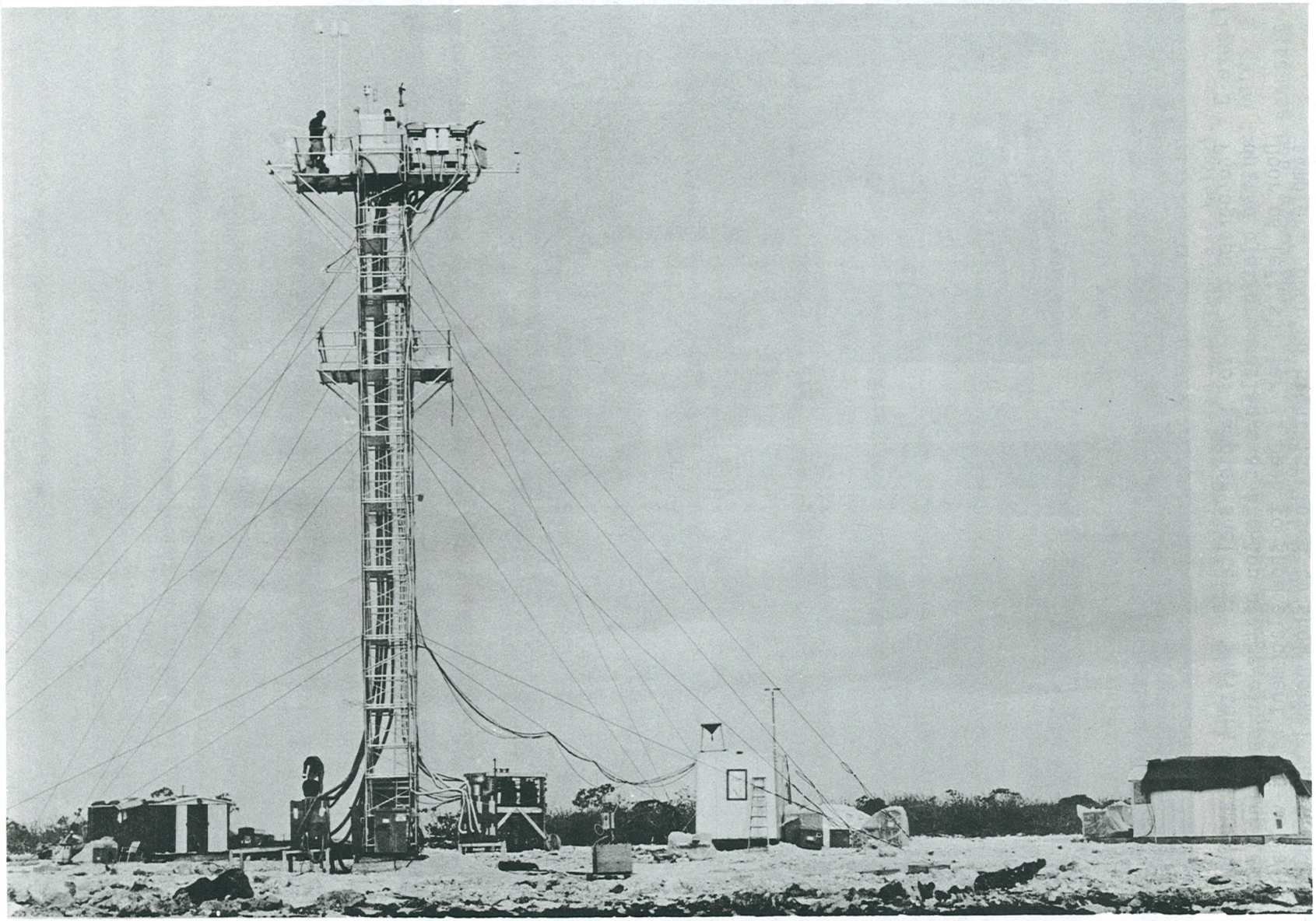

Figure 4 Air sampling tower and associated buildings on Bokandretok island, Enewetak atoll, 1979. Dr. William Fitzgerald, Univ. of Connecticut (at top-level of air sampling tower) shown for scale.

leaks and occasional patching with teflon tape was required to maintain a leak-free system. In Samoa, polyethylene interlocked hose (3" ID, Abbott Rubber Co., Elk Grove Village, IL) was used for the lower half of the ducting string. The interlocked hose provided a more durable connection to the pump and its use at the tower base minimized the possibility of contamination from the phthalate ester plasticizers in the hose. (No contamination has yet been found in the Samoa sample set from the use of this material.) Unfortunately, this hose becomes brittle from long exposure to the sun and cracked after several months use. Rigid aluminum tubing (12' x 3" OD, 0.065" walls, Edgcomb Steel, Slatersville, RI) proved to be an exceptionally durable and contamination free substitute. These were used for the long vertical sections along the side of the tower during our sampling experiments in New Zealand. Individual sections of tubing were joined by butting the ends together inside a sleeve of silicone hose (3" ID, McMaster-Carr Supply Co., New Brunswick, NJ) and sealed with hose clamps. Flexible aluminum ducting was still used at the tower top and bottom where bendable connections were required. An all aluminum rigid tubing system is planned for future experiments. The air samplers will be connected to the hi-vol pumps through a combination of straight sections of aluminum tubing and welded elbows (made from the same tubing) connected with silicone hose.

The sampler was designed for the collection of aerosol samples only or for the simultaneous collection of aerosol and gas phase samples. For aerosol sampling only, the aluminum cartridge is left empty. For gas phase sampling, two polyurethane foam (PUF) plugs are placed inside the cartridge as an adsorbant. A perforated aluminum plate at the bottom of each cartridge prevents slippage of the foam plug into the check-valve. The PUF-plug cartridge can be modified to hold florisil (or any other granular adsorbant) by covering the aluminum plate with a stainless steel screen.

Sampling flowrates were determined by measuring the back-pressure of the pump exhaust through a calibrated orifice (National Environmental Inst., Warwick, RI). Back-pressure *vs.* flowrate calibration curves were obtained for each hi-vol pump and two orifices ("A" for 20-40 $m^3$/hr and

"B" for 60-75 $m^3$/hr) by direct measurement with an American Gas Meter (Model No. AL2300, King-Gaye Engineering Corp., Natick, MA). Typical flow rates obtained during sampling at Enewetak were: 68 $m^3$/hr for GFF only, 25-34 $m^3$/hr for GFF and PUF-plug sampling, and 7-8 $m^3$/hr for GFF and florisil sampling. Following the Enewetak experiment, the flowrates during sampling were adjusted to a pre-selected value by controlling the hi-vol pump speed with a Variac. The pre-selected flowrates were: 68 $m^3$/hr for GFF only and impactor samples, and 34 $m^3$/hr for GFF and 2 PUF-plug samples. Flowrates were recorded twice each day then adjusted as required. The volume of air sampled during the interval between measurements was then calculated by multiplying the average flowrate for the interval times the duration of the interval. An elapsed time meter (designed to run only when the hi-vol pump was actually running) was used to measure the actual sample pumping time. Total sample volume was calculated as the sum of the volumes from each interval.

Cascade impactor: A Sierra Instrument (Carmel Valley, CA) Model 235 five-stage high volume cascade impactor was used. The impactor stages were attached to a modified GFF frame so that an all metal assembly was obtained. The impactor collection substrates (ICSs) and the back-up GFF filter contacted only aluminum or stainless steel. The impactor was mounted on a General Metal Works 8" x 10" filter holder (modified as above) with a 1/8" thick silicone rubber gasket to prevent leakage of air. Impactor and mounting adaptors were customed machined from 316 SS stock (Aurele's Machine Shop, New Bedford, MA). A check valve (as described above) was used between these adaptors to prevent back diffusion of material from the pump and ducting during non-pumping intervals. The complete assembly was mounted inside an all metal shelter (as described above) on the outside of the side railing on the top level platform of the 20 m tower. Like the hi-vol air sampler, the cascade impactor sampler was automatically controlled according to wind speed, wind direction, condensation nuclei counts, precipitation, ozone and radon.

Dry deposition collector: In order to collect samples of dry fallout, a dry deposition collector was constructed which utilized four 20 x 25 cm GFFs as collection substrates. These were held in place with an

aluminum frame (see Figure 5). The collector was secured to a small (~ 1 m) mast mounted on the side railing at the tower top. The collector was carried to the tower top inside an all aluminum box with a tight fitting lid. The lid from the box served to cover the sampler during brief intervals of undesirable winds or precipitation. A vigilant weather watch during collection periods was necessary as sampling was controlled manually.

Rain collector: The rain collector was constructed of two pieces: a 77.5 cm dia. stainless steel mixing bowl (Vollrath Co., Sheboygan, WI) for collecting the rain, and a 55 gal. polyethylene drum (Nalgene labware, Nalge Co., Rochester, N.Y.) for supporting the rain bowl and protecting the collecting flask and lab-jack from wind-driven rain during storms (see Figure 6). A door in the side of the drum allowed access to the 5 L round-bottom flask used to collect the rain sample. An aluminum lid served to protect the rain-bowl from fugitive dust and/or dry fallout contamination during non-sampling intervals. Rain storms were tracked by radar and rain was collected on an event basis. The rain collector cover was removed as the first drops of rain began to fall and the upper level of the tower was evacuated for the duration of the storm. The rain sample was collected immediately after the rain stopped. The rain collector was covered immediately after the rain stopped in order to limit contamination from sea-spray. Then the 5 L flask containing the rain sample was stoppered and carried to the field lab for sub-sampling and extraction; a new, clean 5 L flask was installed, and the sampler was ready for the next rain event.

Pre-extraction of filters and anti-contamination procedures: Because of the extremely low levels of naturally derived organic compounds expected in background aerosol samples, the GFFs, ICSs and PUF-plugs were rigorously cleaned prior to use. For aerosol and dry deposition samples, 20 x 25 cm Gelman type A/E glass fiber filters (Gelman Sciences, Inc., Ann Arbor, MI) were used. For collection of gas phase samples, 125 mm x 72 mm dia. polyurethane foam plugs (Scott polyester-type, white, reticulated, 100 pores/in., 2 lbs./ft.$^3$; obtained from United Foam Plastics Corp., Georgetown, MA) were used. The reticulated polyester-type foam

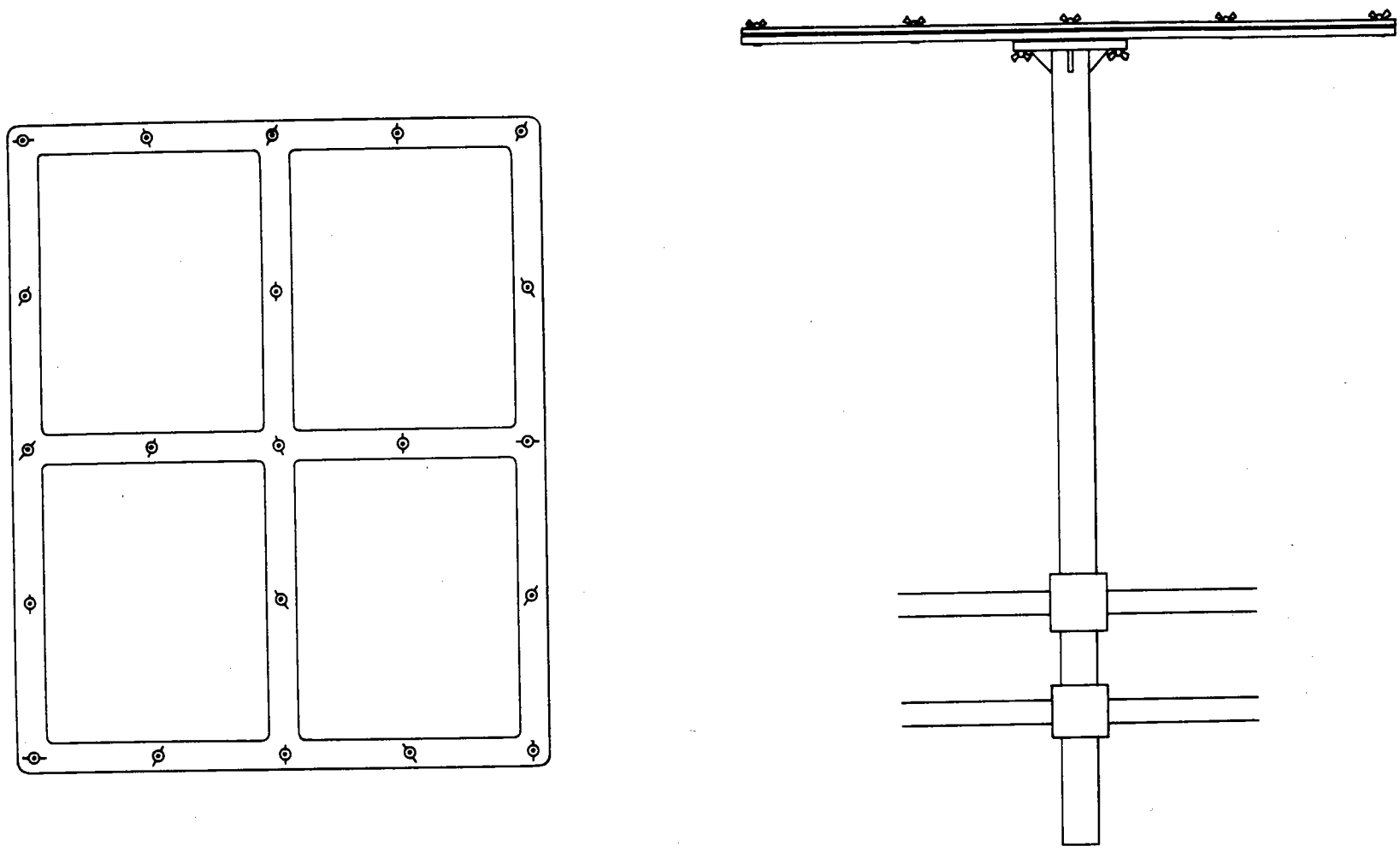

Figure 5 Dry deposition collector. (Left) Top-view of collecting surface showing placement of four GFFs. (Right) Side-view of collector showing mast and rail mountings.

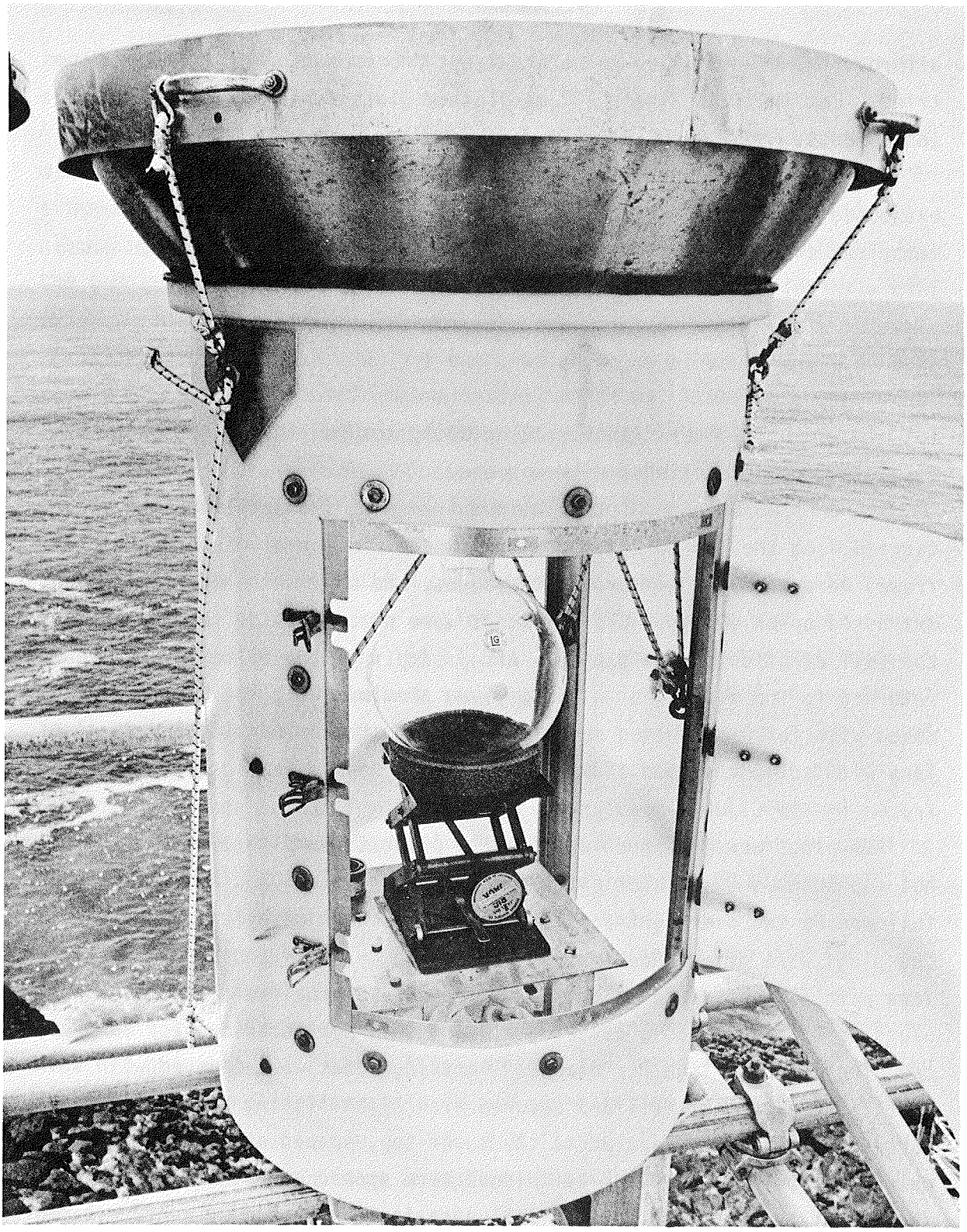

Figure 6 Photograph of rain collector. Door is open to show 5 L rain collecting flask inside base. Normally door is closed to protect flask from rain and sea-spray.

afforded the highest flow rates and least decomposition of all foam types tried. For the ICSs, 143 x 137 mm slotted glass fiber filters (Sierra Instruments, Model No. C-230-GF) were used.

The GFFs were combusted in lots of 5 at 450˚C overnight, then soxhlet extracted for 16-20 hr with 50/50 acetone/methanol, and twice more with methylene chloride. Filters were vacuum dried and placed in clean glass jars with solvent rinsed aluminum foil lined caps for shipment to the sampling site. Four filters were used for each sample. Two GFFs were used as blanks, one in each shelter, and two GFFs were used to collect "duplicate" samples. The fifth filter in each lot served as a spare or a lot blank. All filter transfers (including loading them into the first soxhlet) were accomplished with forceps.

The GFFs were loaded into aluminum frames at the sampling site and carried from the lab to the tower top inside a clean aluminum box. Filter frames were handled only around the edges, and only while wearing solvent extracted nylon gloves. Blank filters were placed inside the shelter for the full duration of the sample. After sampling, the filter frames were returned to the field lab inside a clean aluminum box; the GFFs were removed with forceps, folded several times and stored individually in glass jars with solvent rinsed aluminum foil lined caps. Samples were stored frozen (~ -10˚C) until analysis.

PUF-plugs were cleaned individually prior to sampling by rinsing in hot tap water then soxhlet extracted overnight with 50/50 acetone/methanol, followed by two overnight soxhlet extractions with methylene chloride. The plugs were dried under vacuum at room temperature and stored in glass jars with solvent rinsed aluminum foil caps. At the field site, the PUF-plugs were loaded into a cartridge: two plugs per cartridge for samples, one plug per cartridge for blanks. Cartridge ends were covered with solvent rinsed aluminum foil and secured with tight-fitting plastic end caps. Cartridges were then carried to the tower top, opened and installed as quickly as possible. Blank cartridges were opened and placed inside the shelter standing on end for the full duration of the sample. After sampling, cartridges were sealed as before on the tower top, carried to the field lab where the PUF-plugs were removed from the cartridges and placed

in glass jars. The samples were stored frozen (~ -10˚C) prior to analysis.

The ICSs were combusted in lots of 7 at 450˚C overnight, then soxhlet extracted for 16-20 hr with 50/50 acetone/methanol, followed by two more extractions with methylene chloride. The filters were vacuum dried and placed in clean glass jars with aluminum foil lined caps for shipment to the sampling site. Five filters were used for each impactor sample; one ICS is used for a blank and one ICS is a spare or lot blank. All filter transfers were accomplished with forceps. After the impactor was loaded, it was carried from the field lab to the tower top inside an aluminum box. Impactors were handled only around the edges, and only while wearing solvent extracted nylon gloves. Following sampling, the ICSs were transferred individually to glass jars with solvent rinsed aluminum foil lined caps and stored frozen (~ -10˚C) until analysis.

GFFs for the dry deposition collector were prepared in exactly the same manner as for the hi-vol sampler. Four filters were used per sample; the fifth filter served as a lot blank. After the collector was loaded, it was placed inside an aluminum box and carried to the top of the tower. There it was mounted on top of a short (~ 1 m) aluminum mast. The top of the carrying box serves as a cover for the collector for brief periods of undesirable winds or short rain showers. The collector is removed from the tower for longer durations of undesirable conditions. After sampling, the GFFs are placed inside glass jars with solvent rinsed aluminum foil lined caps and stored frozen (~ -10˚C) until analysis.

Glassware and Reagents: Glass distilled solvents (Burdick and Jackson, Muskegon, MI) were used exclusively. Blanks on individual bottles (1 gal.) of hexane (non-spectro grade) and methylene chloride were run prior to their use. Ethyl acetate and toluene were re-distilled in our lab in an all-glass still (70 cm distillation column filled with raschig rings) prior to use. Aluminum foil and all metal sampling gear were rinsed with acetone then methylene chloride and oven dried. All glassware was washed with 3 percent Micro™ and water, rinsed thoroughly with tap then distilled water, acidic methanol (10 mL 6M HCl + 500 mL methanol), acetone, methylene chloride, and oven dried. Pipettes used

for sample transfers were pre-cleaned by soxhlet extraction overnight with methylene chloride. All glassware was rinsed again with hexane or methylene chloride immediately before use. 6M HCl was prepared by double azeotropical distillation of concentrated HCl [Peltzer, 1979]. 3M HCl was prepared by mixing 100 mL of the doubly distilled 6M azeotrope with 100 mL of permanganate distilled water, then extracting 3 times with 50 mL aliquots of hexane. 0.1M HCl/methanol was prepared by mixing 10 mL of the doubly distilled 6M azeotrope with 250 mL of permanganate distilled water and 250 mL methanol, then extracting four times with 100 mL aliquots of hexane. Acetic anhydride and pyridine were obtained from Applied Science Labs, Inc. (State College, PA). $BF_3$/methanol (14% W/V, Applied Science Labs, Inc.) was extracted three times with hexane (2 mL/5 mL reagent) before use. (Cooling the mixture to -10°C resulted in a more complete phase separation.) The extracted $BF_3$/methanol (1 mL) was then diluted with methanol (4 mL) to give an ~ 3% (W/V) $BF_3$/methanol solution.

Organic compound standards: Standard compounds used for the identification and quantitation of organic compounds in the samples were of the highest purity commercially available. Even carbon number homologs of n-alkanes ($C_{12}$-$C_{36}$), fatty acid methyl esters ($C_{12}$-$C_{26}$), 5α-cholestane, cholesterol and cholesteryl acetate were obtained from Applied Science Laboratories, Inc. Even carbon number homologs of 1-fatty alcohols ($C_{12}$-$C_{30}$), free fatty acids ($C_{12}$-$C_{30}$), n-octacosane, 3-methyltricosane, 1-heptadecanol, 16-methyloctadecanoic acid, methyl nonadecanoate, methyl octacosanoate and methyl triacontanoate were obtained from Analabs, Inc. (North Haven, CT). Nonadecyl docosanoate was prepared from 1-nonadecanol (Research Plus Laboratories, Inc., Bayonne, NJ) and docosanoyl chloride (Sigma Chemical Co., St. Louis, MO). Compound purity and identification were checked by gas chromatography. Octadecyl docosanoate and eicosyl docosanoate (Sigma Chemical Co.) were used as retention time standards and GC/MS reference compounds.

Analytical methodology: A flowchart of the sample analysis is shown in Figure 7. Detailed, step-by-step procedures can be found in the Appendix. Briefly, the procedure is as follows. The samples (GFF, PUF-plug

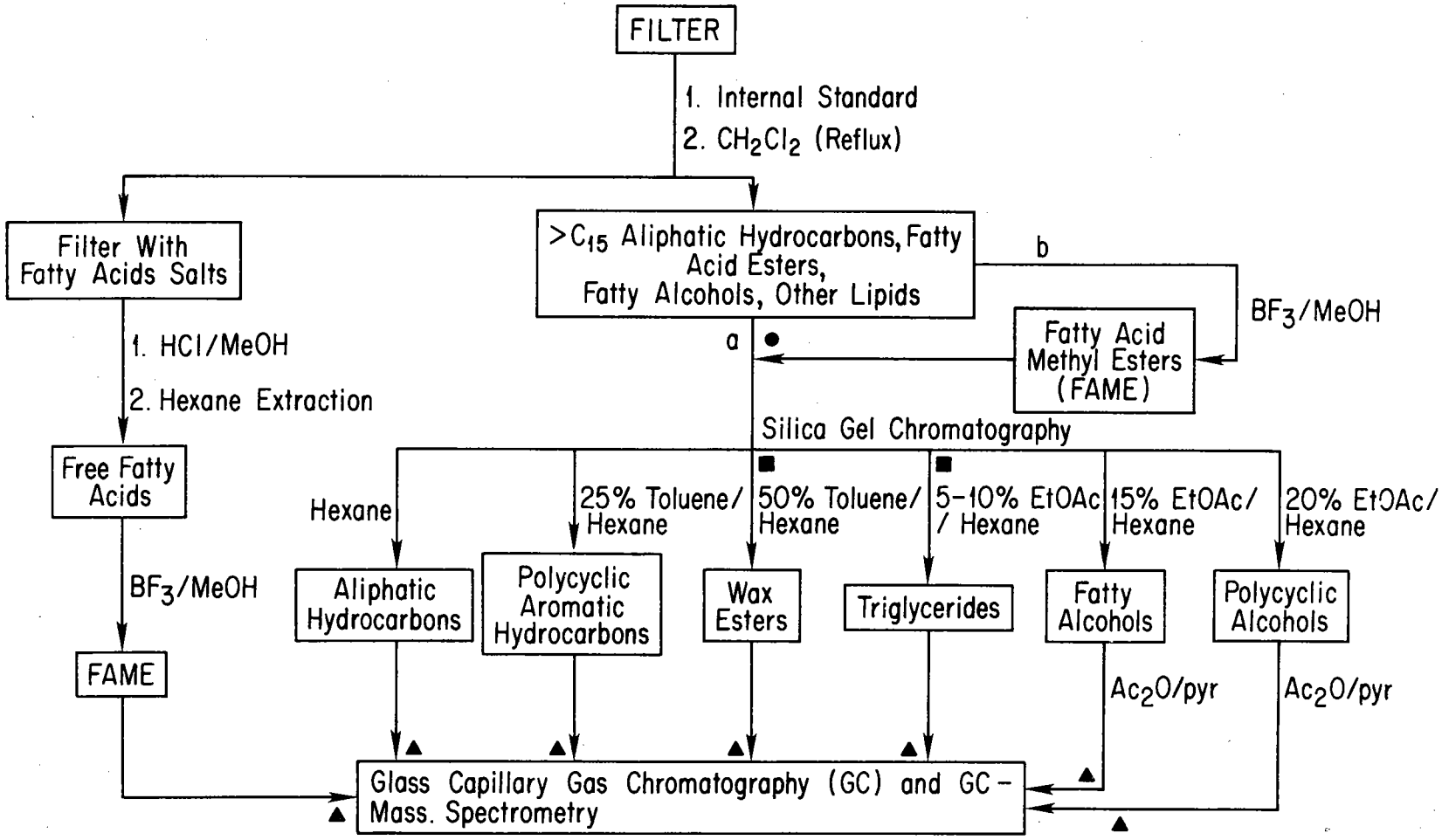


Figure 7 Flowchart of sample analytical scheme. ● Path a or b is followed; path b transesterifies all esters. ■ Path a procedure; for path b, wax ester and triglyceride fractions are combined to give FAME fraction. ▲ Quantitation standard added for GC quantitation.

or ICS) were spiked with a mixture of internal standard compounds and solvent extracted overnight. The extracts were then fractionated by silica-gel chromatography into discrete compound classes. Typically, the total methylene chloride extract was applied to the long column, although some extracts were transesterified with $BF_3$/methanol prior to silica-gel chromatography. For rain samples the methylene chloride extract was split: 75% applied to the column directly; 25% transesterified with $BF_3$/methanol prior to the silica-gel column chromatography. Hydrocarbon, PAH, fatty acid methyl ester and wax ester fractions were analyzed directly by high resolution glass capillary gas chromatography (HRGC). Fatty alcohols and sterols were derivatized prior to HRGC analysis. The acetates were prepared with acetic anhydride, and the fatty alcohol and sterol fractions were purified using a short-column silica-gel chromatography procedure. Combined high resolution glass capillary gas chromatography-mass spectrometry (HRGC/MS) was used to verify peak identifications based on relative retention times and co-injections. The GFFs and ICSs were extracted a second time using hexane following acidification with 0.1M HCl/methanol. These second extracts containing fatty acid salts, were methylated with $BF_3$/methanol then purified using the short-column silica-gel chromatography procedure. The methyl esters were analyzed by HRGC. As before, HRGC/MS was used to verify compound identifications.

GFF extraction: The GFF samples were extracted twice. The first extraction with methlyene chloride yields the extractable lipids; the second extraction with hexane (after acidification of the GFF) yields the fatty acid salts. The filter was broken into small pieces, transferred to a clean 1 L round-bottom flask and 400 mL methylene chloride was added. The solution was spiked with 2-10 µL of recovery standard solution No. 1 containing 3-methyltricosane, fluorene-$d_{10}$, p-terphenyl-$d_{14}$, nonadecyl docosanoate and 1-heptadecanol (50 ng of each compound/µL). For some of the samples, recovery standard solution No. 2 (see below) was added at this time as well. This mixture was refluxed overnight then cooled to ambient temperature and the methylene chloride decanted. The filter was washed 4 times with 50 mL aliquots of methylene chloride. The methylene chloride

decantate and washes were then filtered through a glass frit to remove glass fibers, combined, and concentrated by rotary vacuum evaporation at $\leq$ 20°C to ~ 1 mL. This residue was transferred into a 2 mL screw-cap vial and evaporated to dryness with nitrogen (ultra-high purity, Union Carbide Corporation/Linde Division) at ambient temperature.

For the second extraction, 2-10 µL of recovery standard solution No. 2 containing 16-methyloctacosanoic acid (50 ng/µL) was added at this time (if it had not been added along with recovery standard solution No. 1, see above). The filter was acidified with 100 mL 0.1M HCl/methanol, 100 mL of hexane was added and the mixture was shaken vigorously. After settling, the liquid was filtered and the hexane layer separated. The acidic methanol layer and filter were extracted twice more with 50 mL portions of hexane. The hexane layers were combined and evaporated to dryness as described above.

PUF-plug extraction: The PUF-plugs were spiked with 4 µL of recovery standard solution No. 1 then soxhlet extracted with 2.5 L of methylene chloride overnight. The extract was concentrated by rotary vacuum evaporation at $\leq$ 20°C to ~ 1 mL, then transferred into a 2 mL screw-cap vial and evaporated to dryness as described above.

ICS extraction: The ICSs were extracted in a manner identical to that used for the GFFs except that flask volumes and solvent amounts were halved. A filter was broken into small pieces, transferred to a clean 500 mL round-bottom flask and 200 mL methylene chloride was added. The solution was spiked with 2-10 µL of recovery standard solution No. 1, refluxed overnight, cooled to ambient temperature, and the methylene chloride decanted. The filter pieces were washed 4 times with 25 mL aliquots of methylene chloride. The methylene chloride decantate and washes were then filtered through a glass frit to remove glass fibers, combined, and concentrated by rotary vacuum evaporation at $\leq$ 20°C to ~ 1 mL. The concentrate was evaporated to dryness as described above.

For the second extraction, 2-10 µL of recovery standard solution No. 2 was added. The filter was acidified with 50 mL 0.1M HCl/methanol, 100 mL of hexane was added and the mixture shaken vigorously. After settling, the liquid was filtered and the hexane layer separated. The acidic meth-

anol layer and filter were extracted twice more with 25 mL portions of hexane. The hexane layers were combined and evaporated to dryness.

Rain extraction: Rain samples were spiked with 10-20 μL of recovery standard solution No. 3 containing 3-methyltricosane, n-heptadecan-1-ol, and 16-methyloctadecanoic acid (10 ng of each compound/μL), then acidified with 1 mL 6M HCl per 500 mL of rain water. The sample was then extracted 4 times with methylene chloride and the extract stored at < -10°C until shipment back to the U.S. In the laboratory, the extract was evaporated to dryness. Then the storage bottle and the evaporating flask were rinsed with 0.1M HCl/methanol and then with hexane. The rinses were combined with the extract and centrifuged. The hexane layer, containing the neutral lipids and the free fatty acids, was removed and evaporated to dryness.

Silica-gel chromatography: Sample extracts were fractionated into discrete compound classes by the long-column procedure. Derivatized fractions and the methyl esters of the fatty acid salts were purified by the mini-column procedure. Silica-gel (Bio-Sil A 100/200 mesh, Bio-Rad Laboratories, Richmond, CA) was soxhlet extracted overnight with methylene chloride, vacuum dried, then activated at 225°C for 72 hr. After activation, the silica-gel was cooled in a vacuum desiccator then deactivated by adding permanganate distilled water (5% by wt).

For the long column procedure, 7.00 g of silica-gel were slurried with hexane and transferred quantitatively into a 30 cm x 9 mm, ID chromatography column with a 250 mL solvent reservoir. The hexane was drained from the column and the column was eluted with another 50 mL hexane. The sample extract was dissolved in hexane and transferred to the column. If the sample extract was insoluble in hexane, the extract was dissolved in a small volume of methylene chloride and added to a 25 mL flask containing 70 mg of silica-gel; the sample was coated on the silica-gel by rotary evaporation. The coated silica-gel was slurried with hexane and added to the column. In either case, the column was then eluted with enough hexane to make a total of 20 mL and the eluate collected as the first fraction (L1). The column was then eluted as follows: (L2) 10 mL hexane, 20 mL 25% toluene in hexane; (L3) 20 mL 50% toluene in hexane; (L4) 20 mL 5%

ethyl acetate in hexane, and 20 mL 10% ethyl acetate in hexane; (L5) 20 mL 15% ethyl acetate in hexane; (L6) 20 mL 20% ethyl acetate in hexane; and (L7) 30 mL ethyl acetate and 30 mL methanol. For $BF_3$/methanol treated samples, fractions L3 and L4 were combined (L3 + L4).

For the mini-column procedure, 1.00 g of silica-gel was slurried with hexane and transferred quantitatively into a 125 mm x 6 mm ID chromatography column with a 25 mL solvent reservoir. The hexane was drained from the column and the column eluted with 10 mL hexane. The fraction to be re-chromatographed (L5 or L6 - after acetylation - or the 2nd GFF extract - after $BF_3$/methanol methylation) was dissolved in hexane and added to the column. The column was eluted with enough hexane to make a total of 10 mL and the first fraction (M1) collected. Elution of the minicolumn then proceeds as follows: (M2) 5 mL 25% toluene in hexane; and (M3) 7 mL 5% ethyl acetate in hexane.

Fatty alcohol and sterol acetylation: Fatty alcohols and sterols were acetylated with acetic anhydride and pyridine added directly to the sample vial. The solution is mixed vigorously for 1 min on a Vortex mixer then allowed to stand at room temperature overnight. The reaction was stopped by adding 3M HCl, then extracted 3 times with hexane. The hexane extracts are combined in a 2 mL vial and evaported to dryness with nitrogen. The fatty alcohol and sterol acetates were purified by silica-gel chromatography using the mini-column procedure.

Fatty acid methylation: $BF_3$/methanol was used for the methylation of fatty acids and the transesterification of triglycerides, wax and sterol esters. The sample and $BF_3$/methanol (100 µL of ~ 3% (W/V) were transferred to a pyrex micro-tube, then the micro-tube was purged for 2 min with ultra-high purity nitrogen and sealed with a flame. The reaction mixture was heated at 100°C for 30 min, cooled in an ice-methanol bath, and quantitatively transferred from the micro-tube to a 16 x 100 mm screw-cap culture tube by rinsing three times with methanol and then three times with hexane. This solution was extracted 3 times with hexane, after 1-2 mL of saturated NaCl solution was added. The extracts were combined, concentrated by rotary-vacuum evaporation, transferred to a 2 mL vial and evaporated to dryness with nitrogen. The fatty acid methyl esters (FAMEs)

were purified by silica-gel chromatography using the mini-column procedure.

High resolution glass capillary gas chromatography: n-Alkane (L1), PAH (L2), FAME (L3 + L4 or E2), fatty alcohol (L5) and sterol acetate (L6) fractions were analyzed using either column-A (18-20 m long x 0.32 mm ID glass capillary column coated with SE-52 (0.15 μm) after surface deactivation by persilylation [Grob and Grob, 1980]) in a Carlo Erba Fractovap Model 2150 with a Grob type split/splitless injector used in the splitless mode, or column-B (20 m long x 0.32 mm ID glass capillary column coated with an immobilized film (0.10 μm) of SE-52 [Grob and Grob, 1981]) in a Carlo Erba Fractovap Model 2150 modified to use an air-cooled, septumless, on-column injector. The temperature program for column-A was: 2 min isothermal at 80°C, 4°C/min to 280°C, then hold 280°C for 15 min. A splitless injection period of 45 sec was used. The temperature program for column-B was: 2 min isothermal at 70°C, 5°C/min to 160°C, 3.5°C/min to 290°C, then hold at 290°C for 20 min. Wax ester fractions (L3) were analyzed on column-C (25 m long x 0.32 mm ID glass capillary column coated with an immobilized film of SE-52 [Grob and Grob, 1981]) in a Carlo Erba Fractovap Model 4160 using the air-cooled, septumless, on-column injector. The temperature program for column-C was: on-column injection at 100°C, immediate program of oven to 180°C as quickly as possible, a 3 min hold at 180°C, then 3°C/min to 360°C, and a 20 min hold at 360°C. Hydrogen was used as the carrier gas in all cases; linear gas velocities for columns A, B, and C were 50 cm/sec, 63 cm/sec and 140 cm/sec, respectively. All fractions contained an external standard added to the mixture immediately prior to injection for quantitation purposes. Methyl nonadecanoate was added to the n-alkane fraction (L1), n-octacosane was added to the fatty alcohol acetate (L5), sterol acetate (L6) and fatty acid methyl ester (L3 + L4 or E2) fractions. Electrometer output was recorded with a Linear Instruments Model No. 486 dual-pen chart recorder. Channel one recorded the full potential signal; channel two recorded the signal attenuated by a factor of 10. Peak areas were measured using a Varian Vista Model 401 Chromatography Data System (CDS).

Quantitation: For the purpose of quantifying the organic compounds, two kinds of internal standards were used for each compound class. The quantitation standards were used to determine the amount of each analyte found while the recovery standards were used to measure the percent recovery for the compound class. Compounds of the same class as those being measured but were not normally found in the samples were used as recovery standards. For example, 3-methyltricosane (a-$C_{24}$) was used as the recovery standard for the hydrocarbon fraction. A mixture of recovery standards was added to the samples just prior to the methylene chloride extraction. Quantitation standards contained compounds of another compound class than the one being measured. For example, methyl nonadecanoate (E19) was used as the quantitation standard for the hydrocarbon fraction. Quantitation standards were added to the individual fractions just prior to HRGC analysis. Standards used for each compound class are listed in Table 1.

Table 1. Recovery and quantitation standards.

| Fraction | Compound class | Recovery standard | Quantitation standard |
|---|---|---|---|
| L1 | hydrocarbons | 3-methyltricosane | methyl nonadecanoate |
| L2 | PAHs | fluorene-$d_{10}$<br>p-terphenyl-$d_{14}$ | n-octacosane |
| L3 | wax esters | nonadecyl docosanoate | n-tetracontane |
| L4 | triglycerides (NA) | -- | -- |
| L5 | fatty alcohols | n-heptadecanol | n-octacosane |
| L6 | sterols | n-heptadecanol | n-octacosane |
| L7 | polar lipids (NA) | -- | -- |
| E2 | fatty acid salts | 3-methyloctadecanoic acid | n-octacosane |

NA = not analyzed at this time.

Compound concentrations were determined by first calculating the amount of each analyte found. This amount was then corrected for internal standard recovery. Next, blank levels (corrected for blank internal standard recovery) were subtracted to yield the net amount. Finally, the concentrations of each analyte in the sample were calculated by dividing the net amount by the volume of air or rain sampled. The amount of analyte found was calculated by multiplying the peak-height-ratio or the peak-area-ratio for each individual compound vs. the quantitation standard times the amount of quantitation standard added times the relative response factor. The equations for these calculations are:

$$\text{AMOUNT(X)} = \left[\ \text{AREA(X)/AREA(QS)}\ \right] * \text{AMOUNT(QS)} * \text{RRF}$$

$$\text{CORRECTED AMOUNT (X)} = \text{AMOUNT(X)/INTERNAL STANDARD RECOVERY}$$

$$\text{NET AMOUNT(X)} = \text{CORRECTED AMOUNT(X)} - \text{CORRECTED BLANK AMOUNT(X)}$$

$$\text{CONCENTRATION(X)} = \text{NET AMOUNT(X)/VOLUME OF AIR SAMPLED}$$

where, X is the analyte, QS is the quantitation standard, AMOUNT (QS) is the mass of the quantitation standard in grams added to the compound fraction just prior to gas chromatography, RRF is the relative response factor (see below), and the VOLUME OF AIR SAMPLED is in cubic meters. Internal standard recovery is calculated by dividing the amount of recovery standard found by the amount of recovery standard added. Identical equations can be written for calculations using peak-heights. Typically, we used peak-height-ratios for the calculations for the samples analyzed by splitless injection into the gas chromatograph and peak-area-ratios for samples analyzed by cold, septum-less, on-column injection into the gas chromatograph. Initially, the peak heights were measured by hand, later this was done electronically by a Vista 401 CDS. All peak-areas were integrated electronically by the Vista 401 CDS.

The RRFs were calculated on an area or peak height and mass (not molar) basis relative to the area of peak height and mass of the quantitation standard. Typical RRFs (peak-area based) are listed in Table 2. The RRFs for the n-alkanes based on peak-heights and peak-areas are also shown in Figure 8. The RRFs for the n-alkanes calculated using peak areas

Table 2. Typical relative response factors[+].

| | n-alkanes | fatty acids* | fatty alcohols* |
|---|---|---|---|
| Quantitation Standard | $E_{19}$ | n-$C_{28}$ | n-$C_{28}$ |
| Recovery Standard | a-$C_{24}$ | a-$S_{19}$ | n-$O_{17}$ |
| Recovery Standard RRF | 0.760 | 1.229 | 1.093 |
| Carbon No. | | | |
| 11 | | 1.197 | 1.023 |
| 12 | | 1.202 | 1.038 |
| 13 | | 1.207 | 1.051 |
| 14 | | 1.212 | 1.064 |
| 15 | 0.760 | 1.216 | 1.074 |
| 16 | 0.760 | 1.220 | 1.984 |
| 17 | 0.760 | 1.224 | 1.093 |
| 18 | 0.760 | 1.227 | 1.101 |
| 19 | 0.760 | 1.229 | 1.108 |
| 20 | 0.760 | 1.232 | 1.115 |
| 21 | 0.760 | 1.234 | 1.121 |
| 22 | 0.760 | 1.236 | 1.127 |
| 23 | 0.760 | 1.238 | 1.132 |
| 24 | 0.760 | 1.239 | 1.137 |
| 25 | 0.760 | 1.242 | 1.142 |
| 26 | 0.760 | 1.243 | 1.146 |
| 27 | 0.760 | 1.245 | 1.150 |
| 28 | 0.760 | 1.246 | 1.154 |
| 29 | 0.760 | 1.247 | 1.158 |
| 30 | 0.760 | 1.248 | 1.160 |
| 31 | 0.760 | 1.250 | 1.164 |
| 32 | 0.760 | 1.251 | 1.167 |
| 33 | 0.760 | 1.251 | 1.170 |
| 34 | 0.760 | 1.252 | 1.173 |
| 35 | 0.760 | 1.254 | 1.176 |
| 36 | 0.760 | 1.254 | 1.176 |
| 37 | 0.760 | | |
| 38 | 0.760 | | |
| 39 | 0.760 | Cholesterol | = 0.977 |
| 40 | 0.760 | β-sitosterol | = 0.984 |

+: based on peak areas of equivalent masses with on-column injection.
*: these RRF's were adjusted for the mass of the derivatives; see text.

Standards: $E_{19}$ = methyl nonadecanoate; n-$C_{28}$ = n-octacosane;
a-$C_{24}$ = 3-methyltricosane; a-$S_{19}$ = 16-methyloctadecanoic acid;
n-$O_{17}$ = 1-heptadecanol.

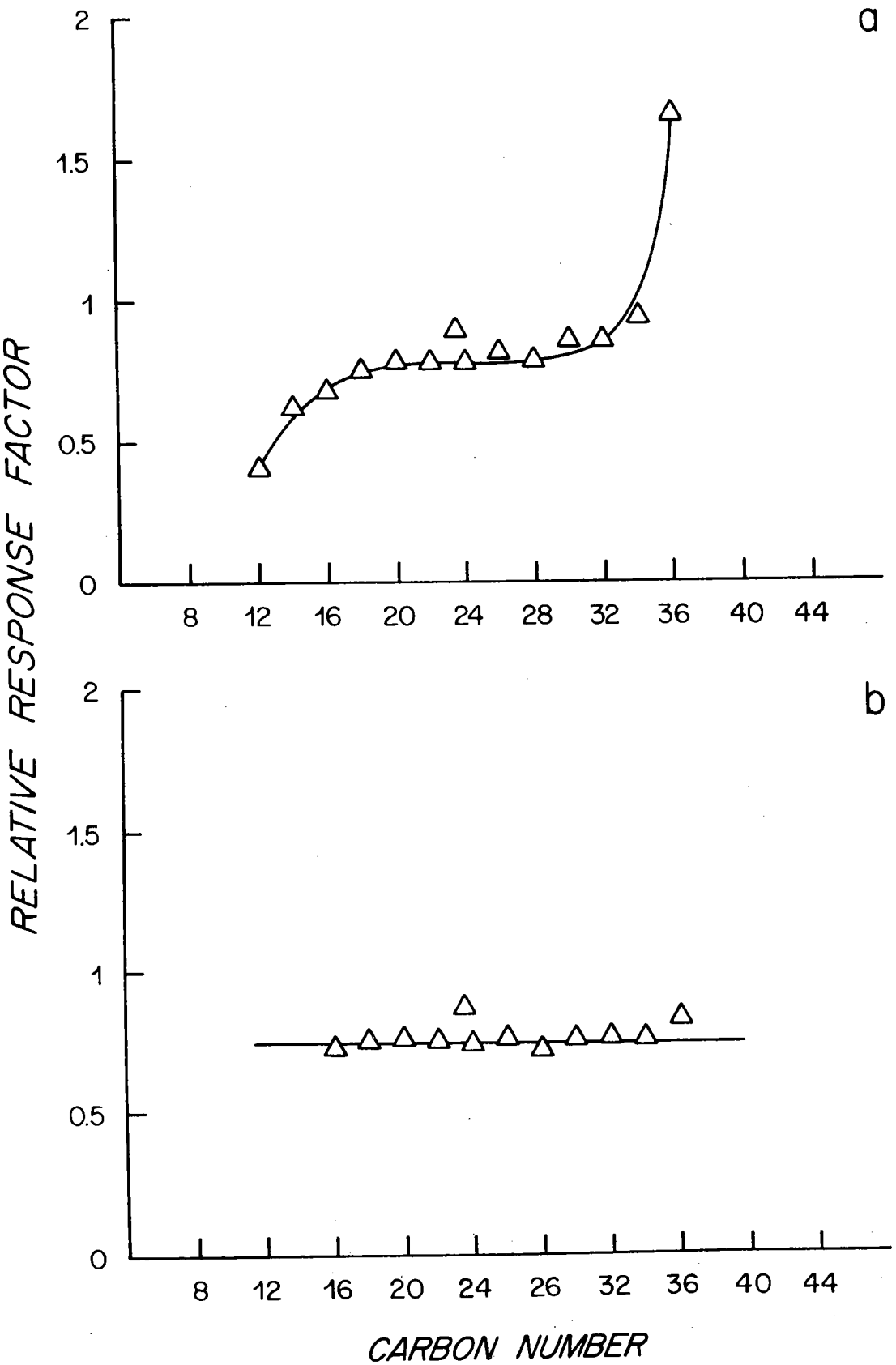


Figure 8 n-Alkane relative response factors. (a) RRFs calculated from peak heights. (b) RRFs calculated from peak areas.

are almost independent of carbon number, while those calculated using peak-heights show a substantial variation from low to high carbon number. This effect is a result of the increase in peak width as a function of retention time and of the discrimination effect at higher carbon number associated with splitless injection [Grob and Grob, 1979]. While the RRFs for the two methods are different, the differences between the results calculated by the two methods were not statistically significant.

The RRFs were determined by injecting a standard solution under normal GC operating conditions. Typically, the standard solution was analyzed in triplicate and the results for each compound were averaged. The solution was prepared using known amounts of the individual homologs from a single compound class as well as the recovery and quantitation standards for this compound class. Not all of the homologs were used to prepare this mixture; generally only the even ones. The RRFs for the odd homologs were then interpolated. For compound classes which require derivatization prior to gas chromatography (e.g., the fatty alcohols and the fatty acid salts), the RRFs were adjusted on a molar basis: known amounts of the derivatized compounds were used to prepare the calibration standard, but the RRFs were calculated for underivatized compounds. Thus, the concentrations calculated using these RRFs are for the underivatized compounds. While this is a small correction for the larger compounds (> $C_{28}$), it can be a 10-20% correction for the lower molecular weight fatty acids and alcohols. The equations for calculating the RRFs and making the derivative adjustment are:

$$RRF(X) = [\ AMOUNT(X)/AMOUNT(QS)\ ] / [\ AREA(X)/AREA(QS)\ ]$$

$$ADJUSTED\ RRF(UC) = RRF(DC)\ *\ [\ MW(UC)/MW(DC)\ ]$$

where, UC is the underivatized compound, DC is the derivatized compound, MW(UC) is the molecular weight of the underivatized compound, and MW(DC) is the molecular weight of the derivatized compound. This single point RRF calibration for each compound assumes a linear RRF relationship (Area (X)/Area (QS) vs. Amount (X)/Amount QS)) with a zero-intercept.

Combined high resolution glass capillary gas chromatography-mass spectrometry: Electron impact mass spectra were initially obtained using a Varian aerograph 1400 gas chromatograph equipped with an SE-52 HT glass capillary column (25 m x 0.32 mm) interfaced to a Finnigan 1015C quadrupole mass spectrometer. Mass spectra were recorded continuously using a Riber 150 data system. Our present HRGC/MS system consists of a Carlo Erba Fractovap Model 4160 gas chromatograph with on-column injector interfaced to a Finnigan Model 4500 quadrupole mass spectrometer. Mass spectra are recorded continuously with an Incos Model 2300 data system. The fused silica capillary column (32 mm long x 0.32 mm ID, DB-5, J & W Scientific, Rancho Cordova, CA) is threaded through the GC/MS interface allowing a direct connection of the GC to the ion source. Helium is used as the carrier gas. All spectra are obtained at 70 eV.

Extract weights: Extracts from the GFFs were dissolved in a small volume of hexane or methylene chloride (250 μL) and a measured portion of this solution (~ 25 μL) was transferred to an aluminum weighing pan with a microliter syringe (Hamilton Co., Reno, NV). After air drying the solution at ~ 40°C, the residue was weighed on a Cahn Model G2 Analytical Electrobalance (Cahn Instruments, Ventron Corp., Cerritos, CA).

## III. RESULTS AND DISCUSSION

The principal goals of this report are to present (i) the capabilities of the analytical method (in terms of a quantitative description of the compound recoveries, GC resolution, etc.), and (ii) the actual results from some samples collected and analyzed as part of our investigation of the long-range atmospheric transport and fluxes of naturally occurring organic compounds across the air/sea interface. Some of our results from Enewetak atoll and American Samoa will be presented as examples of the analytical technique. A more detailed presentation of our results can be found in Gagosian et al. [1981, 1982]; Peltzer et al. [1981]; Peltzer and Gagosian [1983, 1984]; Schneider et al. [1983]; Schneider and Gagosian [1984]; and Zafiriou et al. [1984].

Total lipid extract weights: Typically the extracts were not weighed prior to silica-gel chromatography or HRGC. However, for the two largest samples collected at Enewetak atoll in 1979 we did attempt to weigh the extracts. We did this primarily to test the feasibility of this measurement for truly remote marine samples and secondarily for a comparison with other workers. The weights for these two samples are presented in Table 3 along with the totals for the various compound classes.

It is readily apparent that the levels of methylene chloride extractable lipids are quite low (0.7 - 1.2 ng/m$^3$), and of this ~ 10-25% is identifiable as n-alkanes, n-alkanols and fatty acid esters. The rest of the material is as yet unidentified. On the other hand, the second extract after GFF acidification contained about twice as much extractable material: 1.6 ng/m$^3$ vs. 0.7 ng/m$^3$ and 2.0 ng/m$^3$ vs. 1.2 ng/m$^3$. Of this extract, $\geq$ 50% was identified as n-alkanoic acids, most of which is in the $C_{13}$-$C_{18}$ range.

There is very little data in the literature concerning the total lipid content of remote marine aerosols, and these concentrations vary considerably as a function of the technique used and where the aerosols were collected. Barger and Garrett [1970, 1976] have reported aerosol concentrations for chloroform extractable organic compounds of 700-6300 ng/m$^3$ at Hawaii and 160-4000 ng/m$^3$ in the eastern equatorial Pacific. Simoneit [1977, 1979] reported total neutral lipids for atmospheric aerosols off the west coast of Africa in the range 0.02 - 10 ng/m$^3$ with the highest values, 5-10 ng/m$^3$, for Saharan dusts. However, the nets used for collecting dust samples clearly discriminate against the smaller aerosol particles as collection efficiencies for particles $\leq$ 2 μm are $\leq$ 50% [Simoneit, 1977]. These concentrations are thus best regarded as a lower limit. Indeed, Cox et al. [1982] found 660-6000 ng/m$^3$ total solvent extractable lipids in Harmattan aerosols from Nigeria which are a possible source for some of the samples analyzed by Simoneit [1977]. Eichmann et al. [1980] reported total neutral lipids (as EEOM: ether extractable organic matter) on the order of ~ 800 ng/m$^3$ for the tropical North Atlantic; 700-800 ng/m$^3$ for the Irish west coast (Mace Head and Loop Head); 500 ng/m$^3$ for on-shore only winds at Loop Head, Irish west coast;

Table 3. Extract weights for ENAS-24 and ENAS-33.

| | Sample No. | | | |
|---|---|---|---|---|
| | ENAS-24 | | ENAS-33 | |
| Mid-date | 7.14 | | 7.29 | |
| Volume ($M^3$) | 8500 | | 9200 | |
| | $pg/m^3$ | % | $pg/m^3$ | % |
| Methylene chloride extract | 710 | | 1200 | |
| $C_{21}$-$C_{36}$ n-alkanes | 23 | (3%) | 20 | (2%) |
| $C_{14}$-$C_{32}$ fatty alcohols | 83 | (12%) | 72 | (6%) |
| $C_{13}$-$C_{32}$ fatty acid esters | 69 | (10%) | 40 | (3%) |
| SUM | 175 | (25%) | 132 | (11%) |
| Acidic Methanol/Hexane Extract | 1600 | | 2000 | |
| Fatty acid salts | | | | |
| $C_{13}$-$C_{18}$ | 730 | (46%) | 1400 | (70%) |
| $C_{19}$-$C_{32}$ | 36 | (2%) | 53 | (3%) |
| SUM | 770 | (48%) | 1450 | (73%) |

and 500 $ng/m^3$ for Cape Grim, Tasmania. Clearly, our total neutral lipid concentrations for aerosols collected at the end of the wet season experiment in Enewetak are several orders of magnitude lower than most of the other reported values and are at the lower end of the range reported by Simoneit [1977, 1979].

To the best of our knowledge, there are no reports of fatty acid salt data in the literature from other research groups. Thus there is no basis for comparison with our fatty acid salt data. This is unfortunate, since we found twice as much solvent extractable material and > 90% of the total fatty acids in this fraction for tropical North Pacific aerosols.

Silica-gel chromatography and compound class fractionation: The heart of any analytical method is the ability to resolve and quantitate components. Environmental samples for organic compound analysis present an especially difficult challenge owing to the large number of compounds present with a wide range of molecular weights and their diversity of functional groups. In many cases, the number of components present far exceeds the capabilities of even the best "state-of-the-art" high-resolution glass capillary columns. Even HRGC/MS cannot solve this problem of positively identifying and quantifying all of the compounds in a complex mixture, especially when many of them co-elute. Therefore, as part of the SEAREX program, we have developed an analytical technique for the analysis of trace levels of naturally occurring organic compounds in remote marine aerosols which employs a "pre-separation" of the lipids and waxes into various functional group classes by silica-gel chromatography prior to their analysis by HRGC. The silica-gel chromatography procedure was modified from a method commonly used by marine organic geochemists for the trace analysis of lipids in marine sediments [Lee et al., 1977], plankton and oceanic particulate matter [Wakeham et al., 1980]. This pre-separation avoids the problems of co-eluting compounds during HRGC analysis, thereby simplifying the analysis and eliminating the need for HRGC/MS analysis of all the samples. Since the HRGC analyses are fairly simple, a few representative samples analyzed by HRGC/MS are sufficient to verify the compound identifications based on functional group analysis and HRGC retention times.

The compound classes resolved by the silica-gel chromatography procedure and later analyzed by HRGC are presented in Table 4. Four of the five naturally occurring lipid and wax compound classes of primary interest were completely resolved by this procedure and each was contained within a single fraction. These compound classes are: n-alkanes (L1), wax esters (L3), n-alkan-1-ols/fatty alcohols (L5) and sterols (L6). The fifth compound class (fatty acids) was previously separated from GFF samples as the fatty acid salts by differential extraction. These compounds are essentially insoluble in the first extracting solvent, methylene chloride, and are contained in the second extract (E2, see below). For

Table 4. Compound classes resolved by the long-column silica-gel chromatography procedure.

| Fraction | Compound Classes Found |
|---|---|
| L1 | Saturated and mono-unsaturated hydrocarbons: n-alkanes, iso-alkanes, anteiso-alkanes, cyclo-alkanes, alkenes. |
| L2 | Polycyclic aromatic hydrocarbons (PAHs) |
| L3 | Wax esters, steryl esters |
| L4 | Triglycerides, steroid ketones |
| L5 | Fatty alcohols |
| L6 | Sterols |
| L7 | Polar lipids: phospholipids and glyco-lipids |

rain samples, the fatty acids are extracted along with the non-saponifiable lipids following the acidification of the rain sample. Thus, for the analysis of fatty acids in rain, the sample was split 3:1. The major portion was analyzed as usual; the smaller portion was treated with $BF_3$/methanol yielding the methyl esters of the free fatty acids as well as the FAMEs of esterified fatty acids contained in wax esters, triglycerides, etc.

Initially, when we designed our analytical procedure, only one extraction of the GFF was planned. However, recoveries of the internal standard for fatty acids, 16-methyloctadecanoic acid, were on the order of $\leq$ 1-2%. These very low recoveries led to an important discovery. A second extraction of the GFF with hexane following acidification of the filter with 0.1 M HCl in methanol liberated the fatty acid salts. Internal standard recoveries were 60-80%. Thus we had achieved a quantitative separation of the free fatty acids in their salt form from all the other neutral lipids by differential extraction.

In addition to these five compound classes, several other groups of natural and anthropogenic compounds have been identified within the various fractions. Polycyclic aromatic hydrocarbons, a major anthropogenic contribution to urban atmospheric aerosols, are found in fraction L2; steroid ketones and triglycerides have been isolated in fraction L3 (Gagosian and Smith, 1979; Comita et al., 1984); and several classes of polar lipids, e.g. phospholipids and glycolipids have been found in fraction L7 (Comita and Gagosian, 1983). These later cases were not from atmospheric aerosols but rather from marine sediments, particles filtered from seawater, and marine bacteria. However, their resolution from the other compound classes and presence within a single discrete fraction re-emphasizes the need to pre-separate compound classes prior to HRGC and demonstrates the resolving power of the silica-gel column and its importance to this analytical procedure.

High resolution glass capillary gas chromatography: The separation, identification and quantitation of the individual homologs within each compound class was accomplished by HRGC and HRGC/MS. Actual chromatograms for sample and blank analyses are shown in Figures 9-12 for the n-alkanes, wax esters, fatty alcohols (as acetates) and fatty acid salts (as methyl esters). Most compounds show baseline resolution from other components in the sample. All compound identities were confirmed by comparison of retention times and mass spectra with those for authentic compounds (in no cases were spurious compounds found co-eluting with the major homologs by mass spectrometry). Splitless injection allowed identification and quantitation of $C_{15}$-$C_{36}$ n-alkanes, $C_{11}$-$C_{32}$ fatty alcohols (as acetates) and $C_{11}$-$C_{32}$ fatty acids (as methyl esters). On-column injection expanded our analytical window to: $C_{15}$-$C_{44}$ n-alkanes, $C_{11}$-$C_{40}$ fatty alcohols (as acetates), $C_{11}$-$C_{40}$ fatty acids (as methyl esters) and $C_{39}$-$C_{62}$ wax esters. Based on the total number of compounds resolved in these fractions it is clear that separation and identification of all of these compounds in a single HRGC analysis would not have been possible.

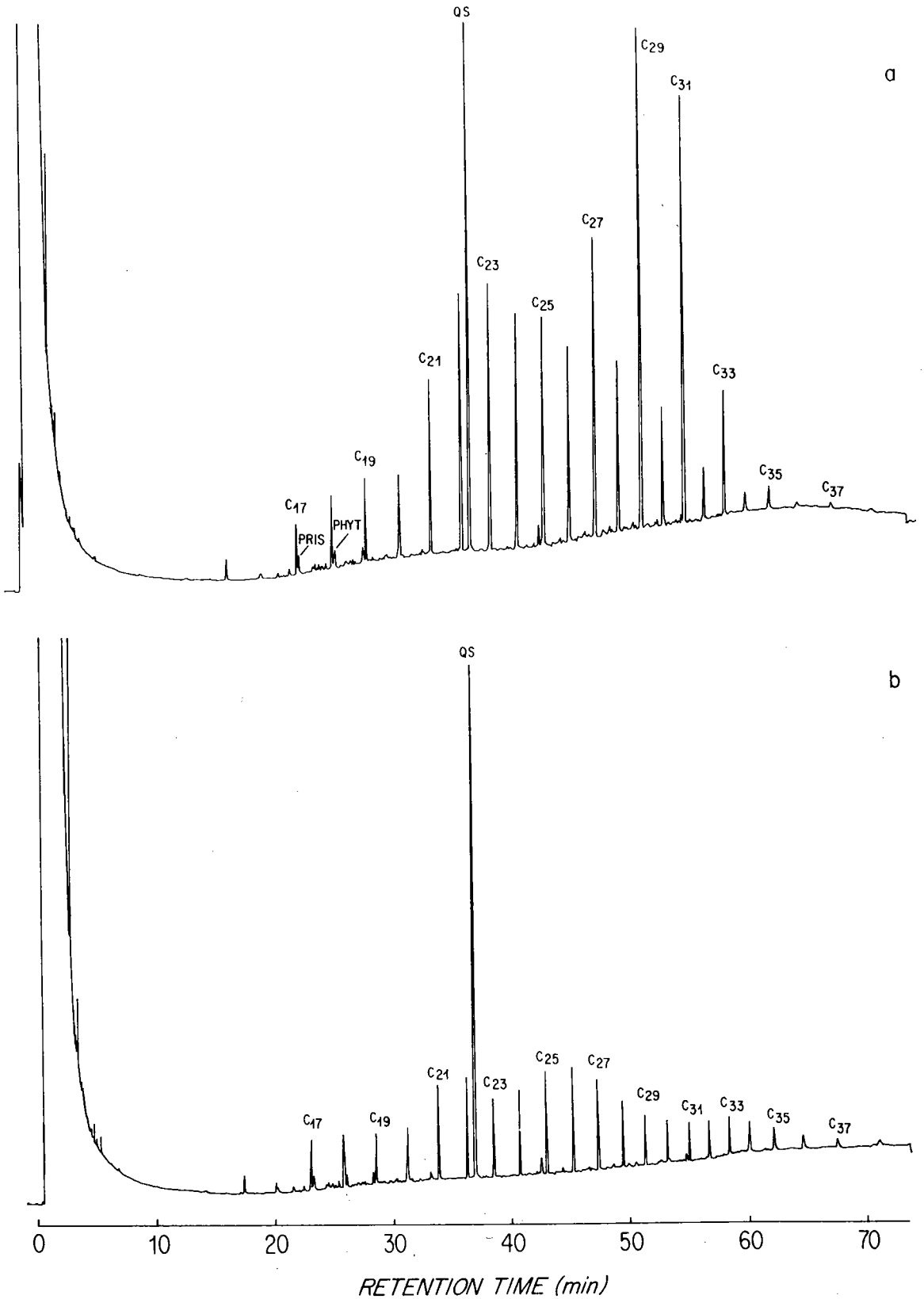


Figure 9 HRGC of n-alkanes. (a) aerosol sample from Enewetak atoll, 1979. (b) blank. Carbon numbers indicate chain length of n-alkanes. PRIS = pristane, PHYT = phytane, QS = quantitation standard: 3-methyltricosane. For GC conditions, see text.

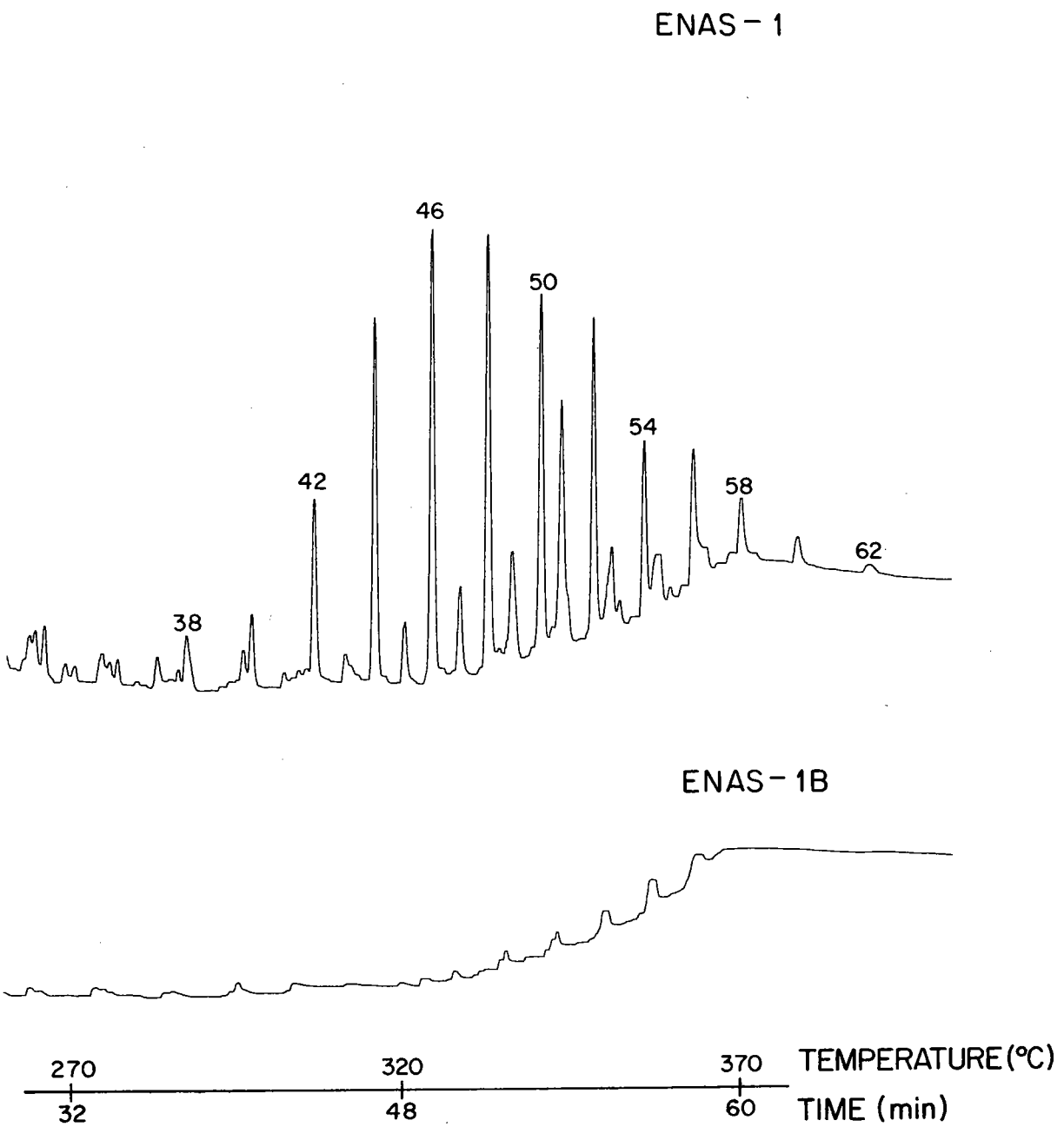


Figure 10 HRGC of wax esters. ENAS-1: aerosol sample from Enewetak atoll, 1979. ENAS-1B: blank. Carbon numbers indicate total chain length (alkyl + acyl) of wax esters. For GC conditions, see text.

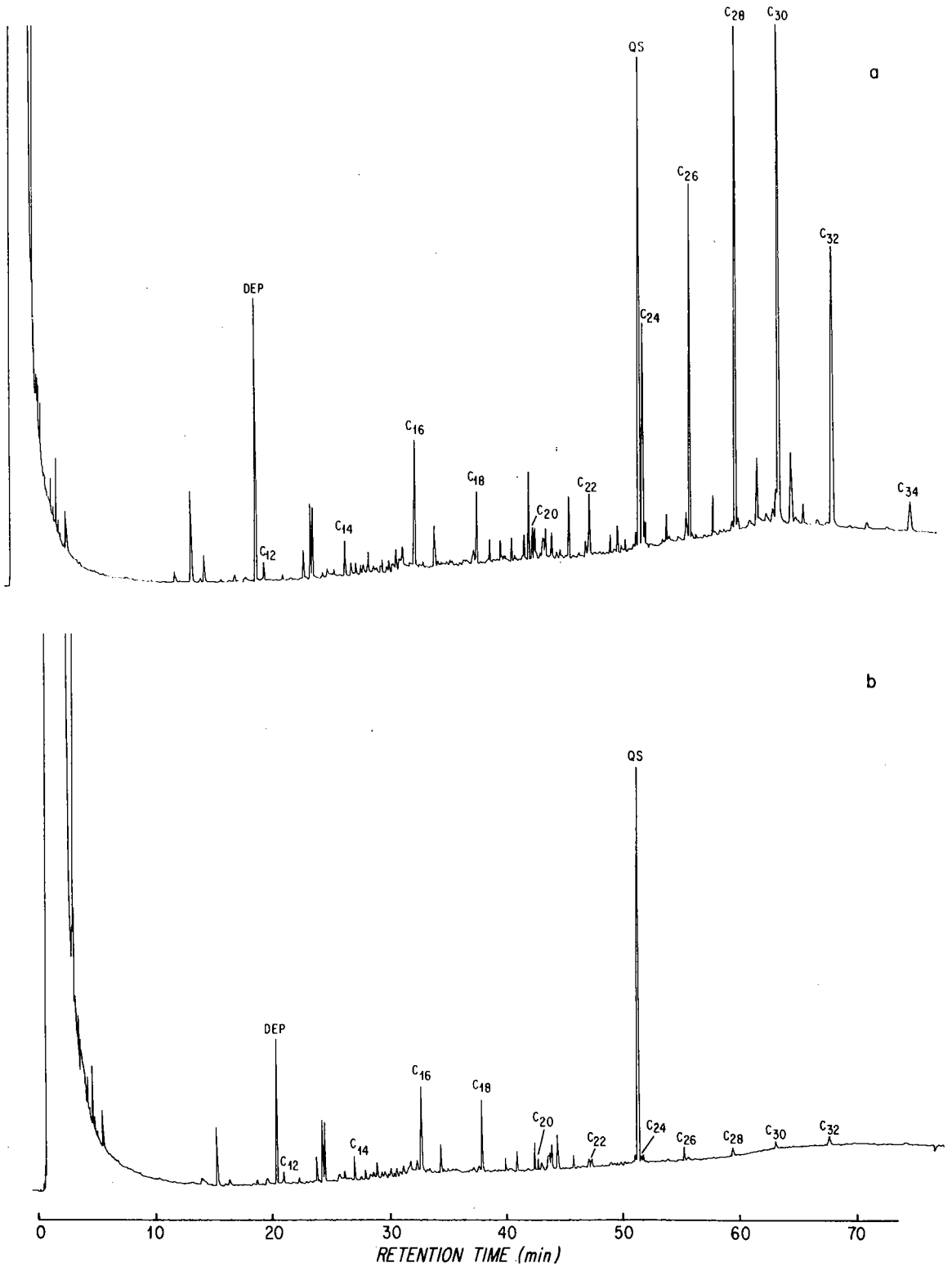


Figure 11 HRGC of fatty alcohol acetates. (a) aerosol sample from Enewetak atoll, 1979. (b) blank. Carbon numbers indicate chain length of alcohol only. DEP = diethyl phthalate, QS = quantitation standard: n-octacosane. For GC conditions, see text.

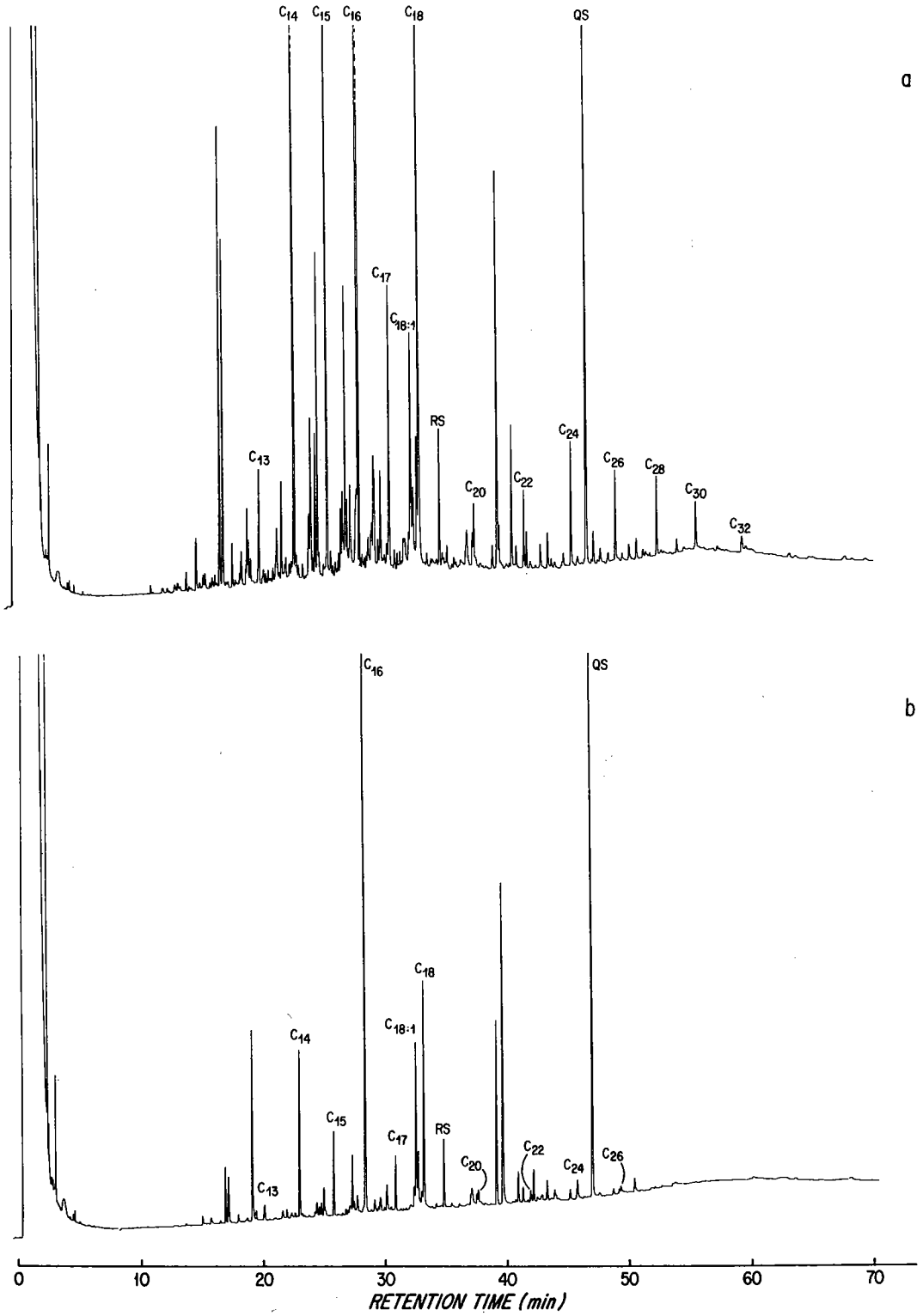


Figure 12 HRGC of fatty acid methyl esters. (a) aerosol sample from Enewetak atoll, 1979. (b) blank. Carbon numbers indicate chain length of fatty acid only. RS = recovery standard: 16-methyloctadecanoic acid, QS = quantitation standard: n-octacosane. For GC conditions, see text.

Recoveries: As we will show, compound recoveries by this analytical method are very good, almost quantitative for some compound classes. This is the result of many contributing factors. It is important to use inert, non-absorbing and non-contaminating materials for the storage and transfer of the samples. Additionally, the derivatization conditions for the fatty alcohol acetates and the fatty acid methyl esters were optimized. In trials using standard compounds, the yields for fatty alcohol acetylation with acetic anhydride were 93.8 $\pm$ 4.7%. The yields for fatty acid methylation were 100.3 $\pm$ 11.3% for saturated compounds and 94.4 $\pm$ 7.4% for unsaturated ones. Transesterification yields for fatty acid esters (wax esters, steryl esters, or triglycerides) were 91.8 $\pm$ 4.8%.

Recoveries of the recovery standards measured for actual samples gives an estimation of the "true recovery" for the method. These recoveries are listed in Table 5. For aerosol samples, recoveries ranged from 63% to 92% with the best recoveries being obtained for n-alkanes and fatty alcohols. For the rain samples the recoveries were lower: 54% to 91%, and the fatty alcohols had the best recovery. The recoveries for the fatty acids (salts) were low in both cases most probably due to their highly surface active nature. Considering the very low levels measured, these recoveries are quite good and were reproducible (s.d. = 10%), but they are not quantitative. Consequently, to avoid errors in quantitation the results must be corrected for internal standard recovery as described above.

In cases where recoveries are less than quantitative (95-99%), it is important to establish that the method does not discriminate against any compound class or between members of a compound class. This determination was made by analyzing a set of filters spiked with a series of known compounds from each compound class at levels equivalent to those found in atmospheric samples from remote marine locations. The four filters used for this experiment were prepared according to the standard method for pre-extracting filters prior to an atmospheric sampling experiment. Three filters were spiked with 2 µl of a mixture of standard compounds containing 40 ng of each compound/µl. The mixture of standard compounds contained 13 n-alkanes, 10 fatty alcohols, 10 fatty acid salts and 2 sterols

Table 5. Mean percent recoveries for recovery standards used in Enewetak atoll and American Samoa aerosol and rain samples.

| Standard | Aerosol samples+ | Rain samples* |
|---|---|---|
| 3-methyltricosane | 91.5 ± 10.3 | 77.3 ± 8.4 |
| n-heptadecanol | 88.8 ± 10.1 | 90.9 ± 7.5 |
| 3-methyloctadecanoic acid | 63.2 ± 11.0 | 54.3 ± 6.4 |

+: mean ± std. dev. of 10 samples.
*: mean ± std. dev. of 8 samples.

to approximate the range of compounds found in a typical sample. The mixture of standard compounds also contained the 3 recovery standards at 50 ng of each standard/μl. A fourth filter was used as a blank and was spiked with a solution containing only the recovery standards. These filters were then analyzed according to the standard procedures described above and listed in detail in the Appendix. The results from the analyses of these filters are listed in Table 6 and are depicted graphically in Figure 13. In contrast to the absolute recoveries of the recovery standards, the recoveries of the individual compounds relative to the recovery standards were essentially quantitative. The mean relative recoveries were: 96.5 ± 2.8% for the $C_{18}$ to $C_{36}$ n-alkanes, 92.5 ± 4.5% for the $C_{14}$ to $C_{30}$ fatty alcohols, 96.4 ± 5.3% for the $C_{20}$ to $C_{30}$ fatty acid salts, 93.3 ± 1.4% for cholesterol and 72.7 ± 2.0% for β-sitosterol.

Within each compound class there is a cut-off point below which the recoveries rapidly drop to zero (see Figure 13), but above this cut-off there is very little discrimination between homologs. The losses at the low end are due to compound evaporation during sample processing, most likely during the nitrogen evaporation step. (Note that while the $C_{12}$ to $C_{18}$ fatty acids were added to the filter, the higher blank levels

Table 6. Recoveries of individual compounds *vs.* recovery standards.

| | Compound Class | | |
|---|---|---|---|
| | Hydrocarbons | Fatty alcohols | Fatty acid salts |
| Recovery standard | 3-methyltricosane | n-heptadecanol | 3-methyloctadecanoic acid |
| Carbon No. | | | |
| 12 | 0.014 ± 0.019 | 0.527 ± 0.051 | |
| 14 | 0.117 ± 0.038 | 0.911 ± 0.129 | |
| 16 | 0.450 ± 0.035 | 0.862 ± 0.084 | |
| 18 | 0.871 | 0.951 ± 0.030 | |
| 20 | 0.909 ± 0.035 | 0.945 ± 0.011 | 0.975 ± 0.087 |
| 22 | 0.975 | 0.930 ± 0.018 | |
| 24 | 1.004 ± 0.060 | 0.961 ± 0.021 | 1.014 ± 0.056 |
| 26 | 0.939 ± 0.014 | 0.975 ± 0.044 | 1.012 ± 0.026 |
| 28 | 0.957 ± 0.013 | 0.920 ± 0.024 | 0.895 ± 0.036 |
| 30 | 0.961 ± 0.025 | 0.873 ± 0.044 | 0.922 ± 0.061 |
| 32 | 0.970 ± 0.001 | | |
| 34 | 1.044 ± 0.030 | | |
| 36 | 1.022 ± 0.055 | | |
| Cholesterol | | 0.933 ± 0.014 | |
| β-sitosterol | | 0.727 ± 0.020 | |
| mean ± s.d. | 0.965 ± 0.028 | 0.925 ± 0.045 | 0.964 ± 0.053 |
| for: | $C_{18}$ to $C_{36}$ | $C_{14}$ to $C_{30}$ | $C_{20}$ to $C_{30}$ |

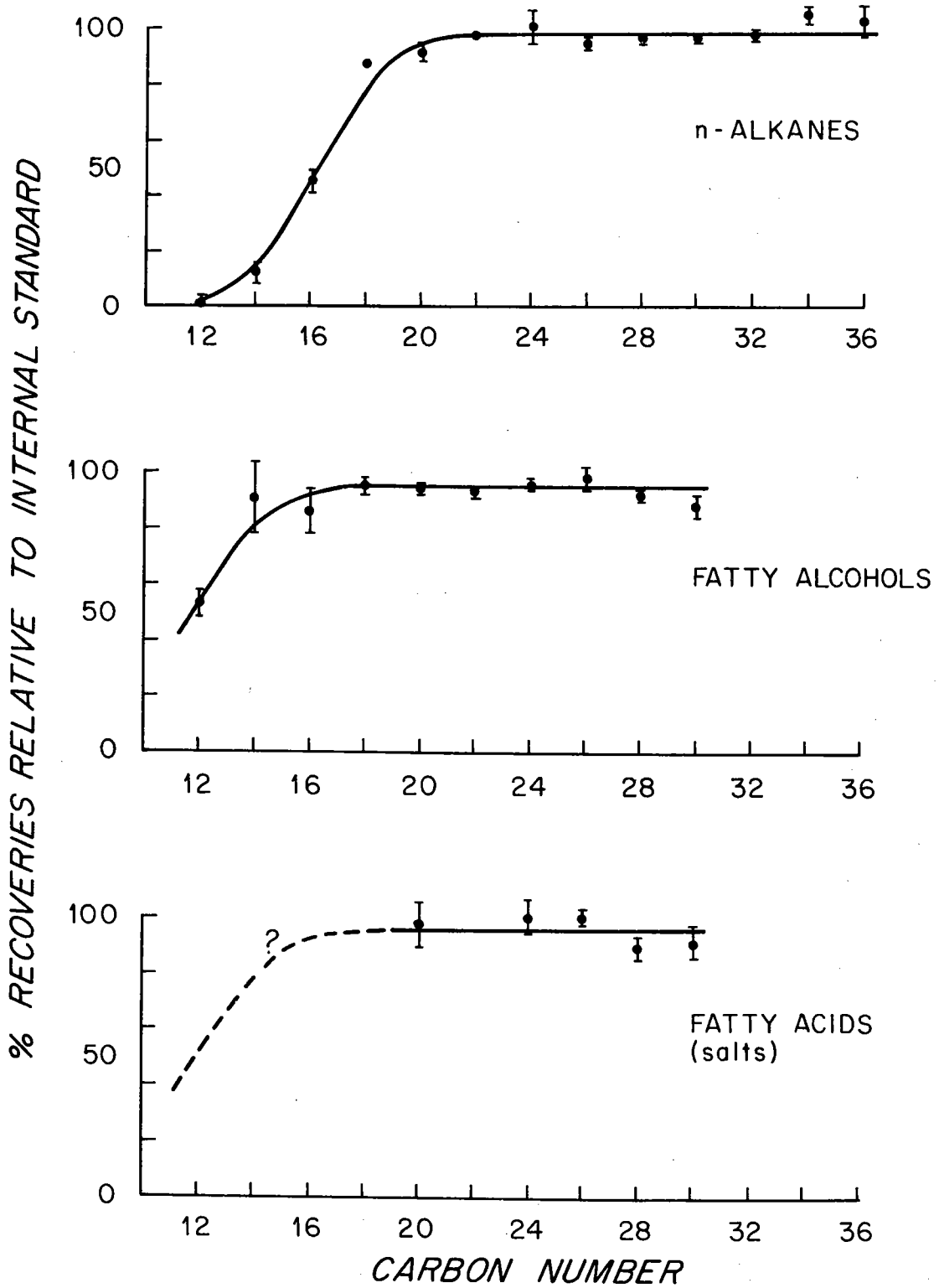


Figure 13 Percent recoveries of individual homologs relative to internal standards.

for these compounds (see below) precluded an accurate determination of their recoveries. For Figure 13, their recoveries were estimated to be the same as the fatty alcohol acetates.) Above about $C_{20}$, the recoveries are high, uniform and very reproducible. For individual homologs, the standard deviations for the three analyses ranged from $\pm$ 0.1% to a high of $\pm$ 12.9%. The mean standard deviations for these analyses were 4.0% overall, 3.0% for the n-alkanes, 4.6% for the fatty alcohols and 5.3% for the fatty acid salts.

If the criterion for the low end for our analytical "window" is chosen as 80% recovery efficiency, then the lower limits for the method are $C_{18}$ for the n-alkanes, $C_{14}$ for the fatty alcohols and $C_{14}$ - $C_{16}$ for the fatty acid salts. Compounds recovered at lower efficiencies will still be detected by this method, but their concentrations will be underestimated by a factor of 2 or more. It is reasonable to assume that the relative recoveries will stay quantitative for the higher homologs beyond the limits of the standards we used, at least up to the upper limits of the gas chromatography procedure due to the non-discriminating nature of "on-column injection" [Galli and Trestianu, 1981]. The relative recoveries for the wax esters were not determined because we lacked the appropriate standards. We estimate that because they are essentially non-volatile and "relatively inert" they will have high recoveries similar to those of the hydrocarbons and fatty alcohols.

We estimated the limits for the range or window of detectability and quantitation of the analytical method as follows: (1)the low end of the range is established by the 50% or 80% recovery level, and (2) the high end is established by the upper limits of the gas chromatography procedures. These limits to our analytical window are listed in Table 7A; typical limits for our reported results are listed in Table 7B.

The less than quantitative recoveries of the internal standards encountered during the recovery trials and during actual sample processing suggested that we may not have been getting complete extraction of the compounds from the glass fiber filters. In order to test this hypothesis and possibly increase our recovery yields, we extracted some of our filters a second time by refluxing overnight in a second aliquot of methylene chloride prior to the acidic methanol/hexane extraction. This second ex-

Table 7. Limits of analytical method windows.

A. Limits of analytical method.

| Compound class | Low end | | High end | |
|---|---|---|---|---|
| | 50% | 80% | splitless | on-column |
| n-Alkanes | $C_{15}$ | $C_{18}$ | $C_{36}$ | $C_{44}$ |
| Wax esters | $C_{12}$ *1 | $C_{16}$ *1 | $C_{42}$ *2 | $C_{62}$ |
| Fatty alcohols | $C_{12}$ | $C_{14}$ | $C_{32}$ | $C_{36}$ - $C_{40}$ *3 |
| Sterols *4 | Cholesterol | Cholesterol | β-sitosterol | β-sitosterol |
| Fatty acid salts | $C_{12}$ | $C_{14}$ | $C_{32}$ | $C_{36}$ - $C_{40}$ *3 |

B. Typical limits of sample results reported

| Compound class | Aerosol | Rain |
|---|---|---|
| n-Alkanes | $C_{21}$ - $C_{32}$ ($C_{40}$) *5 | $C_{15}$ - $C_{36}$ ($C_{40}$) *5 |
| Wax esters | $C_{39}$ - $C_{62}$ | $C_{39}$ - $C_{62}$ |
| Fatty alcohols | $C_{14}$ - $C_{32}$ ($C_{36}$) *5 | $C_{14}$ - $C_{32}$ ($C_{36}$) *5 |
| Sterols | Chlosterol-β-sitosterol. | Cholesterol-β-sitosterol |
| Fatty acid salts | $C_{13}$ - $C_{32}$ ($C_{36}$) *5 | $C_{13}$ - $C_{32}$ ($C_{36}$) *5 |

*1: estimated.
*2: splitless injection of wax esters is not routinely used.
*3: estimated; authentic standards not available.
*4: sterol recovery not limited by volatility or GC column.
*5: numbers in parentheses are upper limits for on-columnn injection only.

traction did not yield any detectable quantities of the neutral lipid compound classes. Therefore we have concluded that a single overnight reflux with methylene chloride is sufficient to recover all the neutral lipids extractable with this solvent, and that the losses observed for the internal standards must be due to absorption or other effects and not due to incomplete extraction.

Methylene chloride is known to slowly decompose to hydrochloric acid. It was thought possible that this small amount of hydrochloric acid may cause decomposition of the wax esters during the GFF reflux step to form free fatty alcohols and fatty acids. In order to test this hypothesis and to compare the extraction efficiency of methylene chloride vs. hexane, we extracted duplicate samples. The two samples used were collected simultaneously under as identical conditions as possible at Enewetak atoll. Wax ester hydrolysis was measured as the amount of n-nonadecanol formed from the hydrolysis of the wax ester internal standard, nonadecyl docosanoate. The results for these two solvents appear to be equal: 3.2% decomposition of the wax ester internal standard was observed for the methylene chloride extract and 5.4% decomposition was observed in the hexane extract. In both cases the amount of decomposition is very small. The results for the other compound classes are summarized in Table 8. For the higher molecular weight fatty alcohols and fatty acid salts, the results of the two extractions are the same; while for the hydrocarbons and lower molecular weight fatty alcohols, the methylene chloride extraction contained approximately 20 - 30% less material than the hexane extract. The total methylene chloride extract contains ~ 85% of that found in the hexane extract. These differences are within our volume uncertainty of $\pm$ 10%. It is worth noting that the blanks for the two different solvents were essentially the same for all compound classes except the hydrocarbons. In this case the methylene chloride blank was about 2 - 3 times more, and this higher blank may account for some of the difference in hydrocarbon concentrations between the two samples.

Thus we have developed a method for the quantitative separation of free fatty acids (as their salts) from the "esterified" fatty acids and the other neutral lipid compound classes by differential extraction. The

Table 8. Methylene chloride *vs.* hexane extraction.

| Compound class | | Methylene chloride pg/m$^3$ | Hexane pg/m$^3$ |
|---|---|---|---|
| Hydrocarbons | $C_{21}$ - $C_{36}$ | 38 (2.2) | 48 (1.8) |
| Wax esters | $C_{39}$ - $C_{62}$ | NA | NA |
| Fatty alcohols | $C_{14}$ - $C_{20}$ | 11 | 3 |
| | $C_{21}$ - $C_{32}$ | 53 (10.1) | 54 (11.9) |
| Sterols | Cholesterol | 1 | 1 |
| | β-sitosterol | 2 | 1 |
| Fatty acid salts | $C_{13}$ - $C_{18}$ | 560 | 880 |
| | $C_{19}$ - $C_{32}$ | 110 (5.6) | 110 (4.2) |
| n-nonadecanol (in blank) | | 2.9 ng | 5.1 ng |
| % decomposition | | 3.2 | 5.4 |

NOTE: (numbers) = CPI.
NA: not analyzed; levels expected would be below detection limit.

fatty acid esters are extracted from the GFF by methylene chloride along with the other lipid compound classes, and the fatty acid salts (which are insoluble in methylene chloride) are extracted from the GFF with hexane following acidification of the filter. The use of internal standards for each compound class allows for both the correction of observed concentrations for the experimental recoveries and the quantitative verification that there is no cross-contamination of fatty acids between fractions. Thus the results for the different compound classes represent biologically and geochemically distinct phases, each with its own inherent source marker and transport mechanism information. It is important that they should be analyzed as such so as to preserve as much of this information as possible.

GFF and rain blanks and detection limits: The ultimate sensitivity of any analysis is determined by the sensitivity of the measuring device. In this case, our gas chromatograph had a sensitivity or instrument detection limit (IDL) of about 0.05 - 0.10 ng. (The IDL was conservatively estimated by multiplying the smallest acceptable peak height by the amount of compound required for a full-scale (f.s.) peak. For example, a 1% f.s. peak was chosen as the smallest detectable peak, and approximately 10 ng of any compound gave a full-scale peak at the most sensitive range and attenuation used, thus 1 % * 10 ng = 0.1 ng. Much smaller peak heights and areas could be detected and accurately measured by the Vista 401 CDS but we selected 0.5% f.s. as a conservative limit.) For a 5000 $m^3$ sample, this corresponds to a theoretical detection limit (or maximum sensitivity) of 0.01 - 0.02 $pg/m^3$. We optimized our utilization of this sensitivity by (1) concentrating the sample to as small a volume as practical prior to injection and then injecting as large a fraction of this as possible into the gas chromatograph (without overloading the column with solvent), and (2) by minimizing the occurrence of the analyte in the blanks.

We have developed handling procedures allowing for approximately one-tenth of the sample to be injected. This is for all practical purposes the upper limit of how much of the sample we can inject. With a maximum injection volume of 2.5 µl, sample volumes smaller than 25 µl would be required in order to inject > 10% of the sample but volumes smaller than 25 µl are exceptionally difficult to handle. Additionally, further concentration of the sample below 25 µl was inadvisable because at this volume we have reached the point where the amount of the analyte in the procedural blanks has become the limiting factor in our efforts to utilize the maximum sensitivity.

The occurrence of the analytes in the procedural blanks was minimized by: (1) using the best grade of contamination-free solvents; (2) developing an elaborate glassware washing and solvent rinsing scheme; (3) scrupulously cleaning and solvent rinsing all equipment prior to use; (4) thoroughly cleaning all sampling media; and (5) paying constant attention to the fact that only the best of laboratory etiquette and anticon-

tamination protocols are acceptable when working with samples. We cannot overemphasize the need for clean solvents throughout this work. Without clean solvents, our procedural blanks would have been at least 10 to 100 times higher for all compounds measured. Burdick and Jackson distilled in glass™ solvents were the cleanest of the six suppliers we tested; the use of only their solvents is specified in our laboratory protocols (see Appendix 1). In order to maintain the lowest possible blank levels, each lot of hexane (non-spectro grade) and methylene chloride was tested prior to purchase, and each individual bottle from these lots was tested for contamination prior to use. Maximum allowable limits are: 200 ng/L for the $C_{21}$-$C_{36}$ n-alkanes with no individual n-alkane to exceed 25 ng/L; and 500 ng/L for phthalate esters with no individual phthalate to exceed 100 ng/L.

For a representative description of the actual blank levels found by this method, we will use the mean blanks for the samples collected during the SEAREX Enewetak atoll and American Samoa field experiments. The mean blanks for the Enewetak aerosol (GFF) and rain samples and the Samoa aerosol (GFF) and rain samples are listed in Tables 9, A and B and Tables 10, A and B, respectively. Actual blank amounts were determined in nanograms, but these have been converted to picograms per cubic meter for aerosol samples by dividing by the typical sample volume of 5000 $m^3$ or to nanograms per liter for rain samples by dividing by a typical sample volume of 1 liter in order to provide the reader with more easily interpretable numbers.

In general the blanks for most compounds were very low, and in many cases they are the lowest procedural blanks for this type of analysis reported in the literature. Even so, for many of the compounds these blank levels are greater than the IDLs. Consequently, the limits of detection (LODs) and the limits of quantitation (LOQs) for these compounds are substantially above the theoretical limits. This "loss of sensitivity" due to the background levels of the analytes in the procedural blanks is the primary reason why so much attention has been devoted to reducing and eliminating contamination.

Table 9A. Mean blanks for Enewetak aerosol samples. *1

| Carbon No. | n-Alkanes pg/m$^3$ | Fatty alcohols pg/m$^3$ | Fatty acid salts pg/m$^3$ |
|---|---|---|---|
| 13 | | | 7 |
| 14 | | 3.1 | 78 |
| 15 | | | 38 |
| 16:0 | | 9.8 | 276 |
| 16:1 | | | 15 |
| 17 | < 0.1 *2 | | 25 |
| 18:0 | < 0.1 *2 | 5.7 | 109 |
| 18:1 | | | 39 |
| 19 | < 0.1 *2 | | |
| 20 | < 0.1 *2 | 1.8 | |
| mean ± s.d. | < 0.1 | 5.1 ± 3.1 | 73 ± 83 |
| median | < 0.1 | 4.4 | 39 |
| 19 | | | < 0.1 *2 |
| 20 | | | < 0.1 *2 |
| 21 | 2.0 | < 0.1 *2 | 0.2 |
| 22 | 2.6 | 1.1 | 11.8 |
| 23 | 4.0 | < 0.1 *2 | 3.4 |
| 24 | 5.9 | 0.7 | 17.6 |
| 25 | 7.8 | < 0.1 *2 | 0.4 |
| 26 | 7.6 | 0.3 | 3.8 |
| 27 | 6.9 | < 0.1 *2 | < 0.1 *2 |
| 28 | 5.2 | 0.1 | 0.4 |
| 29 | 4.0 | < 0.1 *2 | < 0.1 *2 |
| 30 | 3.3 | < 0.1 *2 | < 0.1 *2 |
| 31 | 2.5 | < 0.1 *2 | < 0.1 *2 |
| 32 | 1.9 | < 0.1 *2 | < 0.1 *2 |
| 33 | 1.6 | | |
| 34 | 1.1 | 3.7 (cholesterol) | |
| 35 | 0.8 | | |
| 36 | 0.7 | | |
| mean ± s.d. | 3.6 ± 2.3 | 0.25 ± 0.31 | 3.2 ± 5.4 |
| median | 3.0 | < 0.1 | 0.3 |

*1: calculated by dividing mean blank (ng) by sample volume (5000 m$^3$).
*2: estimated maximum concentration; no detectable peak.

Table 9B. Mean blanks for Enewetak rain samples. *1

| Carbon No. | n-Alkanes ng/L | Fatty alcohols ng/L | Fatty acid salts ng/L |
|---|---|---|---|
| 13 | | | < 2 *2 |
| 14 | | < 0.5 *2 | < 2 *2 |
| 15 | | | < 2 *2 |
| 16:0 | | < 0.5 *2 | < 2 *2 |
| 16:1 | | | < 2 *2 |
| 17 | < 0.5 *2 | | < 2 *2 |
| 18:0 | < 0.5 *2 | < 0.5 *2 | < 2 *2 |
| 18:1 | | | < 2 *2 |
| 19 | < 0.5 *2 | | |
| 20 | < 0.5 *2 | < 0.5 *2 | |
| mean ± s.d. | < 0.5 ± 0.0 | < 0.5 ± 0.0 | < 2 ± 0 |
| median | < 0.5 | < 0.5 | < 2 |
| 19 | | | < 2 *2 |
| 20 | | | < 2 *2 |
| 21 | 2.3 | < 0.5 *2 | < 2 *2 |
| 22 | 7.7 | < 0.5 *2 | < 2 *2 |
| 23 | 18.8 | < 0.5 *2 | < 2 *2 |
| 24 | 38.8 | < 0.5 *2 | < 2 *2 |
| 25 | 44.8 | < 0.5 *2 | < 2 *2 |
| 26 | 48.6 | < 0.5 *2 | < 2 *2 |
| 27 | 39.5 | < 0.5 *2 | < 2 *2 |
| 28 | 30.2 | < 0.5 *2 | < 2 *2 |
| 29 | 20.3 | < 0.5 *2 | < 2 *2 |
| 30 | 16.7 | < 0.5 *2 | < 2 *2 |
| 31 | 9.0 | < 0.5 *2 | < 2 *2 |
| 32 | 5.0 | < 0.5 *2 | < 2 *2 |
| 33 | < 0.5 *2 | | |
| 34 | < 0.5 *2 | < 0.5 *2 (cholesterol) | |
| 35 | < 0.5 *2 | | |
| 36 | < 0.5 *2 | | |
| mean ± s.d. | 18 ± 17 | < 0.5 ± 0.0 | < 2 ± 0 |
| median | 13 | < 0.5 | < 2 |

*1: calculated by dividing mean blank (ng) by sample volume (1 liter).
*2: estimated maximum concentration; no detectable peak.

Table 10A. Mean blanks for Samoa aerosol samples. *1

| Carbon No. | n-Alkanes pg/m$^3$ | Fatty alcohols pg/m$^3$ | Fatty acid salts pg/m$^3$ |
|---|---|---|---|
| 13 | | | 11 |
| 14 | | 1.6 | 340 |
| 15 | 0.21 | | 38 |
| 16:0 | 0.43 | 5.6 | 323 |
| 16:1 | | | 11 |
| 17 | 0.66 | | 21 |
| 18:0 | 0.87 | 8.9 | 90 |
| 18:1 | | | 20 |
| 19 | 0.99 | | |
| 20 | 0.76 | 1.3 | |
| mean ± s.d. | 0.65 ± 0.26 | 4.4 ± 3.1 | 107 ± 132 |
| median | 0.71 | 3.6 | 30 |
| 19 | | | 2.1 |
| 20 | | | 4.2 |
| 21 | 0.80 | 0.10 | < 0.1 *2 |
| 22 | 0.73 | 0.62 | 7.2 |
| 23 | 0.73 | < 0.10 *2 | 1.1 |
| 24 | 0.91 | 0.25 | 8.1 |
| 25 | 0.87 | < 0.10 *2 | < 0.1 *2 |
| 26 | 0.91 | 0.36 | 2.5 |
| 27 | 0.87 | < 0.10 *2 | < 0.1 *2 |
| 28 | 0.68 | 0.80 | < 0.1 *2 |
| 29 | 0.70 | < 0.10 *2 | < 0.1 *2 |
| 30 | 0.55 | 0.42 | < 0.1 *2 |
| 31 | 0.43 | < 0.10 *2 | < 0.1 *2 |
| 32 | 0.38 | 0.10 | < 0.1 *2 |
| 33 | 0.31 | | |
| 34 | 0.26 | 2.4 (cholesterol) | |
| 35 | 0.25 | 1.3 (β-sitosterol) | |
| 36 | 0.22 | | |
| mean ± s.d. | 0.60 ± 0.24 | 0.26 ± 0.23 | 1.9 ± 2.6 |
| median | 0.69 | 0.10 | < 0.1 |

*1: calculated by dividing mean blank (ng) by sample volume (5000 m$^3$).
*2: estimated maximum concentration; no detectable peak.

Table 10B. Mean blanks for Samoa rain samples. *1

| Carbon No. | n-Alkanes ng/L | Fatty alcohols ng/L | Fatty acid salts ng/L |
|---|---|---|---|
| 13 | | | < 0.3 *2 |
| 14 | | 3.0 | < 0.3 *2 |
| 15 | < 0.1 *2 | | < 0.3 *2 |
| 16:0 | < 0.1 *2 | 11.8 | 32.2 |
| 16:1 | | | 7.8 |
| 17 | 2.1 | | < 0.3 *2 |
| 18:0 | 1.4 | 6.4 | 26.6 |
| 18:1 | | | 8.8 |
| 19 | 2.4 | | |
| 20 | 1.8 | 1.3 | |
| mean ± s.d. | 1.3 ± 0.9 | 5.6 ± 4.0 | 8.4 ± 11.1 |
| median | 1.6 | 4.7 | 3.5 |
| 19 | | | < 0.3 *2 |
| 20 | | | 6.7 |
| 21 | 1.8 | < 0.3 *2 | < 0.3 *2 |
| 22 | 3.0 | 0.5 | 20 |
| 23 | 5.6 | < 0.3 *2 | < 0.3 *2 |
| 24 | 11.0 | 0.3 | 20 |
| 25 | 14.0 | < 0.3 *2 | < 0.3 *2 |
| 26 | 14.3 | 0.3 | 6.7 |
| 27 | 10.3 | < 0.3 *2 | < 0.3 *2 |
| 28 | 7.5 | 2.1 | < 0.3 *2 |
| 29 | 5.4 | < 0.3 *2 | < 0.3 *2 |
| 30 | 2.6 | 2.0 | < 0.3 *2 |
| 31 | 1.9 | < 0.3 *2 | < 0.3 *2 |
| 32 | 1.2 | < 0.3 *2 | < 0.3 *2 |
| 33 | 0.9 | | |
| 34 | < 0.3 *2 | 7.5 (cholesterol) | |
| 35 | < 0.3 *2 | 1.9 (β-sitosterol) | |
| 36 | < 0.3 *2 | | |
| mean ± s.d. | 5.0 ± 4.8 | 0.6 ± 0.6 | 4.1 ± 7.3 |
| median | 2.8 | < 0.3 | < 0.3 |

*1: calculated by dividing mean blank (ng) by sample volume (1 liter).
*2: estimated maximum concentration; no detectable peak.

The detection limits for the specific compounds of interest were determined individually. According to the recommendations of the ACS Subcommittee on Environmental Analytical Chemistry [MacDougall et al., 1980], the LOD is 3 times the standard deviation of the blank. Likewise, the LOQ was recommended as 10 times the standard deviation of the blank. Thus the blank levels of the individual analytes and the variability of these levels is essential information for calculating the LODs and LOQs for the compounds of interest. In our experience, the major source of each compound in the blank came from the extraction solvent. Very little if any material could be attributed to the GFF or the glassware used in the procedure. Since the same bottle and amount of solvent was used for the extraction of a sample filter and its companion blank filter, there was very little variation between the amount of each compound measured in the blank and that contributed to the sample by the extraction solvent. However, since we were only able to extract four filters (sample or blank) per bottle of solvent, it was not possible to calculate the variability of the blank in a meaningful way with any kind of statistical treatment of the data. Instead, we obtained an estimate of the analytical uncertainty by assuming that the mean of the standard deviations from the analysis of the individual compounds in the recovery experiment (described above) is representative of the variability of this method.

The analytical uncertainties for the various compound classes are listed in Table 11. Each compound class is divided into two carbon number ranges based on their biological distribution, levels of occurrence and reproducibility of recovery. The lower carbon number range is generally restricted to marine derived compounds while the higher carbon number range contains compounds of primarily terrestrial plant wax origin. This division also corresponds to a difference in the analytical uncertainty of the measurements. The marine-derived compounds, being lower in molecular weight, were more volatile and more difficult to analyze. Hence, they tended as a group to be more variable analytically. Thus, for each group of compounds the mean of the individual standard deviations as measured during the recovery experiment (see Table 6) was used as our best approximation of the analytical uncertainty ($\sigma$) of the result. These uncertainties (expressed as a percentage of the blank) then

Table 11. Analytical uncertainties, LODs and LOQs for Enewetak atoll and American Samoa aerosol and rain samples.

| | n-Alkanes | Fatty alcohols | Fatty acid salts |
|---|---|---|---|
| Carbon no. range | $C_{17}$ - $C_{20}$ | $C_{14}$ - $C_{28}$ | $C_{13}$ - $C_{18}$ |
| mean s.d. | 3.5% | 6.1% | N.M. |
| LOD | 10% | 20% | 30% |
| LOQ | 35% | 60% | 100% |
| Carbon no. range | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean s.d. | 2.8% | 2.5% | 5.3% |
| LOD | 10% | 10% | 15% |
| LOQ | 30% | 25% | 50% |

LOD and LOQ are expressed as a percentage of the blank.
N.M.: not measured.
s.d.: standard deviation.

determine the limits of detection and quantitation: LOD = 3$\sigma$ and LOQ = 10$\sigma$. For simplicity, these limits were rounded to the nearest 5%. The actual limits used for the Enewetak and Samoa sample sets are listed in Table 11 as a percentage of the blank. Then for each sample the limits for the individual compounds were calculated by simply multiplying the appropriate percentage times the procedural blank for that sample. For example, the mean LOD for n-nonacosane in the Enewetak aerosol set was 10% * 4.0 pg/m$^3$ = 0.40 pg/m$^3$, and the mean LOQ for n-nonacosane was 30% * 4.0 pg/m$^3$ = 1.20 pg/m$^3$. The mean LODs and LOQs are summarized in Table 12 for the Enewetak atoll sample set, and again in Table 13 for the American Samoa sample set.

Like the mean blanks from which these limits are derived, the limits of detection and quantitation for this method are very low, however they

Table 12. LODs and LOQs for Enewetak samples.

| A. Aerosol samples | n-Alkanes pg/m$^3$ | Fatty alcohols pg/m$^3$ | Fatty acid salts pg/m$^3$ |
|---|---|---|---|
| 1. LOD: | $C_{17}$ - $C_{20}$ | $C_{14}$ - $C_{20}$ | $C_{13}$ - $C_{18}$ |
| mean ± s.d. | | 1.0 ± 0.6 | 22 ± 25 |
| median | < 0.01 | 0.9 | 12 |
| range | | 0.4 - 2.0 | 2 - 83 |
| | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean ± s.d. | 0.36 ± 0.23 | 0.03 ± 0.03 | 0.5 ± 0.8 |
| median | 0.30 | < 0.10 | 0.06 |
| range | 0.07 - 0.78 | < 0.01 - 0.11 | < 0.02 - 2.6 |
| 2. LOQ: | $C_{17}$ - $C_{20}$ | $C_{14}$ - $C_{20}$ | $C_{13}$ - $C_{18}$ |
| mean ± s.d. | | 3.0 ± 1.8 | 73 ± 83 |
| median | < 0.04 | 2.6 | 39 |
| range | | 1.1 - 5.9 | 7 - 280 |
| | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean ± s.d. | 1.1 ± 0.7 | 0.06 ± 0.08 | 1.6 ± 2.7 |
| median | 0.9 | 0.03 | 0.19 |
| range | 0.2 - 0.3 | < 0.03 - 0.28 | < 0.05 - 8.8 |

| B. Rain samples | n-Alkanes ng/L | Fatty alcohols ng/L | Fatty acid salts ng/L |
|---|---|---|---|
| 1. LOD: | $C_{17}$ - $C_{20}$ | $C_{14}$ - $C_{20}$ | $C_{13}$ - $C_{18}$ |
| mean ± s.d. | | | |
| median | < 0.05 | < 0.1 | < 0.06 |
| range | | | |
| | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean ± s.d. | 1.8 ± 1.7 | | |
| median | 1.3 | < 0.05 | < 0.3 |
| range | < 0.05 - 4.9 | | |
| 2. LOQ: | $C_{17}$ - $C_{20}$ | $C_{14}$ - $C_{20}$ | $C_{13}$ - $C_{18}$ |
| mean ± s.d. | | | |
| median | < 0.18 | < 0.3 | < 2.0 |
| range | | | |
| | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean ± s.d. | 5.4 ± 5.1 | | |
| median | 3.9 | < 0.13 | < 1.0 |
| range | 0.15 - 15 | | |

Table 13. LODs and LOQs for Samoa samples.

| A. Aerosol samples | n-Alkanes pg/m$^3$ | Fatty alcohols pg/m$^3$ | Fatty acid salts pg/m$^3$ |
|---|---|---|---|
| 1. LOD: | $C_{15}$ - $C_{20}$ | $C_{14}$ - $C_{20}$ | $C_{13}$ - $C_{18}$ |
| mean ± s.d. | 0.07 ± 0.03 | 0.88 ± 0.62 | 32 ± 40 |
| median | 0.07 | 0.72 | 9 |
| range | 0.02 - 0.10 | 0.26 - 1.78 | 3 - 100 |
| | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean ± s.d. | 0.06 ± 0.02 | 0.03 ± 0.02 | 0.29 ± 0.39 |
| median | 0.07 | 0.01 | < 0.02 |
| range | 0.02 - 0.09 | < 0.01 - 0.08 | < 0.02 - 1.2 |
| 2. LOQ: | $C_{15}$ - $C_{20}$ | $C_{14}$ - $C_{20}$ | $C_{13}$ - $C_{18}$ |
| mean ± s.d. | 0.23 ± 0.09 | 2.6 ± 1.9 | 110 ± 130 |
| median | 0.25 | 2.2 | 30 |
| range | 0.07 - 0.35 | 0.8 - 5.3 | 11 - 340 |
| | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean ± s.d. | 0.18 ± 0.07 | 0.07 ± 0.06 | 1.0 ± 1.3 |
| median | 0.21 | 0.03 | < 0.05 |
| range | 0.07 - 0.27 | < 0.03 - 0.20 | < 0.05 - 4.0 |

| B. Rain samples | n-Alkanes ng/L | Fatty alcohols ng/L | Fatty acid salts ng/L |
|---|---|---|---|
| 1. LOD: | $C_{15}$ - $C_{20}$ | $C_{14}$ - $C_{20}$ | $C_{13}$ - $C_{18}$ |
| mean ± s.d. | 0.13 ± 0.09 | 1.1 ± 0.8 | 2.5 ± 3.3 |
| median | 0.16 | 0.94 | 1.0 |
| range | 0.01 - 0.24 | 0.26 - 2.4 | < 0.1 - 9.7 |
| | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean ± s.d. | 0.50 ± 0.48 | 0.06 ± 0.06 | 0.62 ± 1.10 |
| median | 0.28 | < 0.03 | < 0.05 |
| range | 0.03 - 1.43 | < 0.03 - 0.21 | < 0.05 - 3.0 |
| 2. LOQ: | $C_{15}$ - $C_{20}$ | $C_{14}$ - $C_{20}$ | $C_{13}$ - $C_{18}$ |
| mean ± s.d. | 0.46 ± 0.32 | 3.4 ± 2.4 | 8.4 ± 11.1 |
| median | 0.56 | 2.8 | 3.5 |
| range | < 0.04 - 0.84 | 0.8 - 7.1 | < 0.3 - 32 |
| | $C_{21}$ - $C_{36}$ | $C_{21}$ - $C_{32}$ | $C_{19}$ - $C_{32}$ |
| mean ± s.d. | 1.5 ± 1.4 | 0.15 + 0.15 | 2.1 ± 3.6 |
| median | 0.84 | < 0.08 | < 0.15 |
| range | 0.09 - 4.3 | < 0.08 - 0.53 | < 0.15 - 10 |

are still not as low as is theoretically possible (0.01 - 0.02 pg/m$^3$ for aerosols or 0.05 - 0.10 ng/l for rain). The IDL can only be achieved by reducing the levels of the analytes in the procedural blanks. Unfortunately, a further reduction of these blank levels does not appear to be possible at this time as it will require a one to two orders of magnitude reduction in the level of contaminants in the extraction solvents. The mean LODs for the Enewetak aerosol samples were 0.4 $\pm$ 0.2 pg/m$^3$ for the $C_{21}$ - $C_{36}$ n-alkanes, 1.0 $\pm$ 0.6 pg/m$^3$ for the $C_{14}$ - $C_{20}$ fatty alcohols, 0.03 $\pm$ 0.03 pg/m$^3$ for the $C_{21}$ - $C_{32}$ fatty alcohols, 22 $\pm$ 25 pg/m$^3$ for the $C_{13}$ - $C_{18}$ fatty acid salts and 0.5 $\pm$ 0.8 pg/m$^3$ for the $C_{19}$ - $C_{32}$ fatty acid salts. Since the blank for the wax esters was essentially negligible, the LODs for these compounds were equal to the IDL of 0.01 - 0.02 pg/m$^3$. Analogous detection limits were obtained for the Enewetak rain ramples. For the Samoa sample set, even lower LODs were obtained for the $C_{21}$ - $C_{36}$ n-alkanes (0.06 $\pm$ 0.02 pg/m$^3$), while the LODs for the fatty alcohols and fatty acid salts remained about the same. For either sample set, these LODs are the lowest detection limits reported in the literature for any analytical method (aerosol or rain) of this type, and they represent the cumulative results of an extensive effort in this laboratory to reduce and control sample contamination and procedural blanks.

The limits of quantitation used were approximately three times the limits of detection. A summary of the actual limits used can be found in Tables 12 and 13 for the Enewetak and Samoa sample sets respectively. These limits, like the LODs, were very low and are the lowest values reported in the literature. Consequently, of the 86 naturally occurring organic compounds that we have chosen to study in remote marine aerosols, > 90% were found at levels > = the LOQ, and another 5% were found at levels exceeding the LOD but not the LOQ. A few compounds, notably the lower molecular weight n-alkanes and fatty alcohols, were not detected. For compounds whose concentrations are just above the LOQ the uncertainty in the concentration is $\pm$ 30% ($10\sigma \pm 3\sigma$) at the 99% confidence level. As the concentration increases above the LOQ, the uncertainty of the concentration approaches the uncertainty in the air volume measurement (estimated as $\pm$ 10%).

PUF-plug blanks and detection limits: The procedural blank for the gas phase compounds was much different from that for either the aerosol or rain samples. The gas phase compounds were "trapped" by adsorption on the surface of the PUF-plugs. This material was substantially different than the GFF in terms of its inherent blank and our ability to clean it. The plugs were by their very nature much more contaminated than the GFF. Despite an exhaustive extraction procedure, we were unable to obtain a good blank. Most of this contaminating material was "polymeric" and resulted in 50 - 100 μl of a yellow oil upon rotary evaporation of the extract. This oil did not dissolve in hexane which made it very difficult to transfer the extract residue to the silica-gel chromatography column so a special procedure was developed. The residue was redissolved in methylene chloride and 70 mg of silica-gel was added to the flask. The suspension was then rotary evaporated until a free flowing powder resulted. The extract residue was now evenly coated on the surface of the silica gel and by slurrying this in hexane it could be transferred quantitatively to a silica-gel chromatography column. Internal standard recoveries by this procedure were > 95%. Fortunately, none of this oily material was eluted in the first fraction although it did elute in later fractions.

The plugs required ~ 3 L of methylene chloride per extraction, and this in itself was a major source of n-alkanes in the blank. The mean n-alkane blank levels are listed in Table 14. In addition, the LOD and LOQ for each n-alkane is also listed. The analytical uncertainty used for calculating the LODs for gas phase n-alkanes was estimated as twice the analytical uncertainty for the aerosol n-alkanes. The LOQ for the gas phase n-alkanes was estimated in a similar fashion. As in the case of the aerosol samples these blanks and limits of detection and quantitation are calculated in terms of concentration by assuming a standard sample size of 5000 $m^3$. In general these blank levels and limits are approximately 3 - 10 times greater than those for the aerosol samples. However, they are still quite low and have allowed us to make a reasonable determination of the levels of gas phase hydrocarbons in the remote marine atmosphere [Zafiriou et al., 1984].

Table 14. Blank concentrations, LODs and LOQs for gas phase n-alkanes.

| n-Alkane pg/m$^3$ | Blank pg/m$^3$ | LOD pg/m$^3$ | LOQ |
|---|---|---|---|
| $C_{15}$ | N.D. | 0.04 *1 | 0.12 *2 |
| $C_{16}$ | N.D. | 0.04 *1 | 0.12 *2 |
| $C_{17}$ | < 0.3 | < 0.06 | < 0.21 |
| $C_{18}$ | 0.9 | 0.2 | 0.6 |
| $C_{19}$ | 0.8 | 0.2 | 0.6 |
| $C_{20}$ | 0.5 | 0.1 | 0.4 |
| mean $\pm$ s.d. | 0.6 $\pm$ 0.2 | 0.1 $\pm$ 0.1 | 0.3 $\pm$ 0.2 |
| $C_{21}$ | 0.7 | 0.1 | 0.4 |
| $C_{22}$ | 1.9 | 0.4 | 1.1 |
| $C_{23}$ | 4.9 | 1.0 | 2.9 |
| $C_{24}$ | 11.3 | 2.3 | 6.8 |
| $C_{25}$ | 15.6 | 3.1 | 9.4 |
| $C_{26}$ | 16.0 | 3.2 | 9.6 |
| $C_{27}$ | 11.2 | 2.2 | 6.7 |
| $C_{28}$ | 7.0 | 1.4 | 4.2 |
| $C_{29}$ | 4.1 | 0.8 | 2.5 |
| $C_{30}$ | 2.6 | 0.5 | 1.6 |
| $C_{31}$ | 1.4 | 0.3 | 0.8 |
| $C_{32}$ | 0.6 | 0.1 | 0.4 |
| $C_{33}$ | 0.3 | 0.06 | 0.2 |
| $C_{34}$ | 0.2 | 0.04 | 0.1 |
| $C_{35}$ | 0.1 | 0.04 *1 | 0.1 *2 |
| $C_{36}$ | < 0.1 | 0.04 *1 | 0.1 *2 |
| mean $\pm$ s.d. | 4.9 $\pm$ 5.5 | 1.0 $\pm$ 1.1 | 2.9 $\pm$ 3.3 |

N.D.: not detected; below instrument detection limit of 0.02 pg/m$^3$.
*1: estimated as 2 x IDL.
*2: estimated as 6 x IDL.

General blank problems: Our efforts to achieve as low a procedural blank as possible led us to try several different schemes for cleaning the GFFs prior to sampling. A variety of methods are described in the literature including: no treatment [Barbier et al., 1981], combustion only [Simoneit, 1980; Simoneit and Mazurek, 1982], solvent extraction only [Barger and Garrett, 1970; Van Vaeck et al., 1979; Chesselet et al., 1981; Marty and Saliot, 1982], or a combination of solvent extraction and combustion techniques [Ketseridis et al., 1976; Eichmann et al., 1979]. We achieved our best results by extracting the GFFs overnight with 50/50 acetone/methanol followed by two overnight extractions with methylene chloride. After the solvent extractions, the filters were dried at room temperature inside a vacuum desiccator connected to a water aspirator through a molecular sieve trap. Vacuum drying was found to be a cleaner process than air drying inside a standard laboratory convection oven even when the filters were protected from dust during the latter process.

For most compound classes solvent extraction alone is sufficient to clean the GFFs prior to sampling. However, the fatty acid salts are not removed by this process. We combusted the GFFs prior to solvent extraction in an effort to lower the blank for these compounds. By comparing the procedural blanks for the GFFs used in Samoa (combusted vs. uncombusted) we found that for the combusted filters the mean blank is 50% higher than for the uncombusted filters. Chesselet et al., [1981] reported similar results when comparing the two processes for total organic carbon. Given that the combustion step tends to make the GFFs somewhat brittle and difficult to handle, solvent extraction alone is the pre-cleaning method of choice.

Although the use of polyethylene bags to store and transport GFFs has been commonly used by other workers [Barger and Garrett, 1970; Ketseridis et al., 1976; Eichmann et al., 1979, 1980], we have found that the use of solvent rinsed polyethylene bags to store and transport GFFs prior to and after sampling resulted in exceptionally high blanks. During the SEAREX Pigeon Key Testing experiments, we found that "blank" filters stored in polyethylene bags contained twice the amount of methylene chloride extractable organic matter as was found in the sample filters. Further-

more, GC analysis of this extract exhibited a large, broad, unresolved complex mixture (UCM) with few discernable peaks. On the other hand, we have found that transporting the GFFs in glass jars with foil-lined lids results in procedural blanks which are indistinguishable from blanks done on GFFs immediately after the initial solvent clean-up extraction.

Polycyclic aromatic hydrocarbons: In addition to the five naturally occurring lipid compound classes that we measured, the method is also capable of separating, identifying and quantifying PAHs. These compounds are contained within a discrete fraction from the silica-gel column chromatography: fraction L2 (see Table 4). The GC column used for all the other analyses was also used to separate and identify the PAHs. Typically this column provides baseline resolution of all the major PAHs from fluorene to coronene, as shown in Figure 14. Two deuterated compounds were chosen as recovery standards for this compound class: fluorene-$D_{10}$ and p-terphenyl-$D_{14}$. The quantitation standard, n-octacosane, was chosen because it has the same response factor as the PAHs. The National Bureau of Standards Standard Reference Material 1649 (SRM-1649: Urban Dust/Organics) was used to check recoveries and quantitation of these compounds by our method. Additionally, we analyzed SRM-1648 (Urban Particulate Matter) for an idea of the compositional variability of urban dust. Both samples were extracted with methylene chloride in an ultrasonic bath and centrifuged to remove suspended particles. The methylene chloride extract was then processed in a manner exactly analogous to that for the GFFs. The results of these experiments are reported in Table 15. For the five PAHs whose concentrations were certified by NBS, we found essentially the same concentrations by our method. Concentrations of the other five compounds were in good agreement with the NBS results as well. These results clearly demonstrate the usefulness of this method for the detection and quantitation of PAHs in atmospheric particulate matter.

Typical sample results: The results from the analysis of the Enewetak sample set are summarized in Table 16. Column 1 lists the dry season mean aerosol concentrations; column 2 lists the wet season mean aerosol concentrations; column 3 lists the mean gas phase concentrations for both seasons; and column 4 lists the mean concentrations for lipids in rain. The

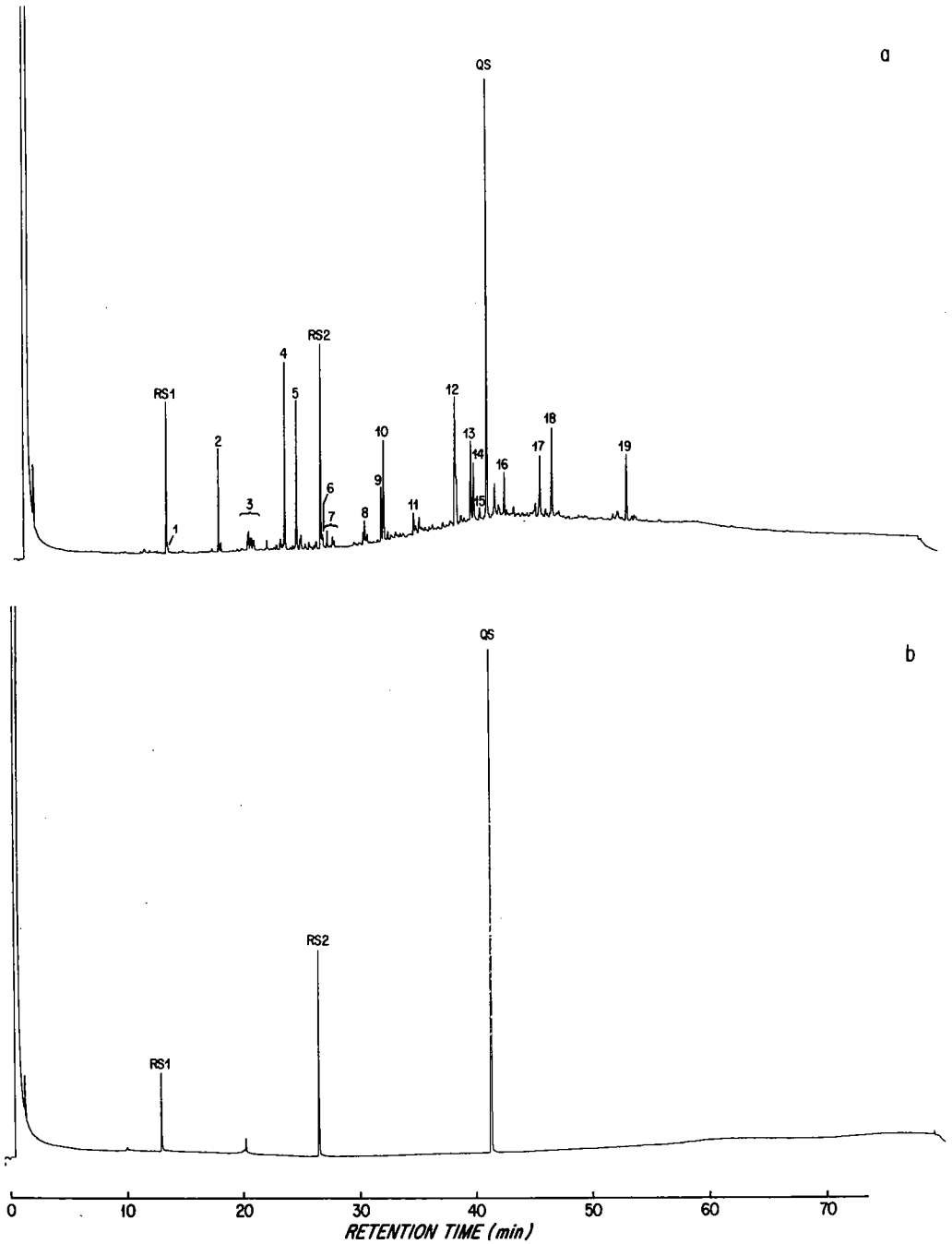


Figure 14 HRGC of polycyclic aromatic hydrocarbons. (a) Urban dust sample SRM-1644. (b) procedural blank. 1 = fluorene, 2 = phenanthrene, 3 = methylphenanthrenes, 4 = fluoranthene, 5 = pyrene, 6 = p-terphenyl, 7 = methlypyrenes, 8 = benzo[ghi]-fluoranthene, 9 = benz[a]anthracenes, 10 = chrysene/triphenylene, 11 = methylbenz[a]anthracenes, 12 = benzofluoranthenes, 13 = benzo[e]pyrene, 14 = benzo[a]pyrene, 15 = perylene, 16 = m-quaterphenyl, 17 = indeno[1, 2, 3-c,d]pyrene, 18 = benzo[ghi]-perylene, 19 = coronene, RS1 = recovery standard-1: fluorene-$^{d}10$, RS2 = recovery standard 2: p-terphenyl-$^{d}14$, QS = quantitation standard; n-octacosane. For GC conditions, see text.

Table 15. Polycyclic aromatic hydrocarbons in urban dust.

| Compound | SRM-1649 | | SRM-1648 |
|---|---|---|---|
| | NBS µg/g | WHOI µg/g | WHOI µg/g |
| Phenanthrene | 4.5 | 3.58 | 3.28 |
| Fluoranthene* | 7.1 ± 0.5 | 7.60 | 8.00 |
| Pyrene | 6.6 | 6.72 | 6.59 |
| Benz[a]anthracene* | 2.6 ± 0.3 | 2.74 | 2.82 |
| Chrysene | 3.6 | 5.06 | 7.92 |
| Benzo[e]pyrene | 3.3 | 4.16 | 6.34 |
| Benzo[a]pyrene* | 2.9 ± 0.5 | 3.51 | 3.16 |
| Perylene | 0.76 | 0.96 | 1.02 |
| Indeno[1,2,3-cd]pyrene* | 3.3 ± 0.5 | 3.38 | 4.88 |
| Benzo[ghi]perylene* | 4.5 ± 1.1 | 4.89 | 6.10 |

*: NBS certified concentrations, others listed for information only.

Table 16. Summary of Enewetak sample analyses.

| | Aerosol samples D.S. *1 pg/m$^3$ | Aerosol samples W.S. *2 pg/m$^3$ | Gas Phase *3 pg/m$^3$ | Rain Samples *4 ng/L |
|---|---|---|---|---|
| n-Alkanes | | | | |
| Sum $C_{17}$ - $C_{20}$ | 1.0 | 0.6 | 28 | 27 |
| Sum $C_{21}$ - $C_{36}$ | 99 | 32 | 320 | 104 |
| CPI $C_{21}$ - $C_{36}$ | 2.8 | 2.0 | 1.2 | 1.1 |
| UCM | ND | ND | 1300 | 1500 |
| Wax esters | | | | |
| Sum $C_{39}$ - $C_{62}$ | 59 | NA | | NA |
| CPI $C_{39}$ - $C_{62}$ | 8.5 | NA | | NA |
| Fatty alcohols | | | | |
| Sum $C_{14}$ - $C_{20}$ | 3.3 | 7.4 | | 68 |
| Sum $C_{21}$ - $C_{32}$ | 140 | 65 | | 20 |
| CPI $C_{21}$ - $C_{32}$ | 10 | 14 | | > 4 |
| Sterols | | | | |
| Cholesterol | 3.3 | 2.9 | | 34 |
| β-sitosterol | ND | ND | | 10 |
| Fatty acid salts | | | | |
| Sum $C_{13}$ - $C_{18}$ | 2900 | 960 | | 1430 |
| Sum $C_{19}$ - $C_{32}$ | 380 | 70 | | 130 |
| CPI $C_{19}$ - $C_{32}$ | 2.4 | 4.8 | | 4.4 |
| Total *5 | 3600 | 1100 | 350 | 1800 |

NA = not analyzed; ND = not detected.
*1: D.S. = dry season mean concentrations.
*2: W.S. = wet season mean concentrations.
*3: mean of 3 samples.
*4: mean of 6 samples.
*5: excluding UCM (unresolved complex mixture).

individual compound results have been presented in detail elsewhere (for aerosol results see: Gagosian et al. [1981, 1982]; for rain and gas phase results see: Zafiriou et al. [1984]), and we will only briefly discuss these results here. The obvious decrease in hydrocarbon, wax ester, fatty alcohol and high molecular weight fatty acid salts during the wet season reflects the seasonal nature of dust storm activity in China and changes in the wind fields over the North Pacific ocean [Duce et al., 1980, 1983; Uematsu et al., 1983]. In general, the levels of identifiable organic compounds we report (1-4 ng/m$^3$) are lower than any previously reported in the literature. Much higher levels of organic compounds have been reported for aerosols collected off the coast of Africa. Simoneit [1980] found up to 10 ng/m$^3$ of n-alkanes, fatty acids and fatty alcohols; while Marty and Saliot [1982] found 6-13 ng/m$^3$ of n-alkanes alone. In both cases, the organic material in these aerosols was dominated by waxes of terrestrial origin. Van Vaeck et al. [1979] also found naturally derived organic compounds (~ 30 ng/m$^3$) in aerosols collected at coastal North Atlantic sites. They reported the presence of anthropogenic compounds (~ 5 ng/m$^3$) in these samples as well, but the n-alkane and fatty acid distributions were still dominated by terrestrial plant waxes. Eichmann et al. [1979, 1980] found quite a different distribution for n-alkanes in aerosol samples collected in the North Atlantic and Indian oceans. They reported very high levels (~ 5-50 ng/m$^3$) of predominantly anthropogenic n-alkanes. Barger and Garrett [1976] found levels of fatty acids (3-300 ng/m$^3$) in aerosols collected over the eastern equatorial Pacific ocean which are much greater than the levels we have reported for aerosols collected at Enewetak atoll. Finally, Schneider et al. [1983] and Schneider and Gagosian [1984] found terrestrial plant waxes in aerosols collected off the coast of Peru at levels ~ 3-5 fold higher than our Enewetak results. We attribute the differences between our results and those of other workers to differences in sampling locations and proximity to sources, especially with regards to the presence of anthropogenic compounds. However, we find the great similarity between the n-alkane compositions and concentrations reported by Eichmann et al. [1979, 1980] for the North Atlantic and Indian oceans to be very puzzling, since one would

expect the Indian ocean samples to represent a more remote marine location.

It is interesting to note that while the authors listed above all report n-alkane concentrations, and some report fatty alcohol, fatty acid and PAH concentrations, none have reported fatty acid salt concentrations. All the fatty acid concentrations reported by other authors were for fatty acids obtained following hydrolysis/saponification of an organic solvent filter extract and thus represent esterified fatty acids, i.e. triglycerides, wax and steryl esters, etc., and not the free fatty acids which exist in the salt form on the GFFs. Thus, our fatty acid salt concentrations are not directly comparable to the reported fatty acid ester concentrations. For the Enewetak samples, we have found that while the fatty acid salts have a composition similar to the fatty acid esters, these two compound classes have important differences. Most important of these differences is the fact that the fatty acid salt concentrations are as much as 10 times higher; and for some samples, the identifiable fatty acid salts represent ~ 50% of the total solvent extractable organic matter [Gagosian et al., 1982]. This makes them the singly most abundant compound class yet found.

In Figure 15, the compositions of the four major compound classes are shown for a typical Enewetak aerosol sample. This sample was collected at the height of a dust event and thus represents the strongest terrestrial source signature. Based on the carbon number ranges and the carbon preference index (CPI) of the n-alkanes, wax esters and fatty alcohols found, the source of the lipids is clearly the epicuticular waxes of terrestrial vascular plants. Whether this material is emitted directly to the atmosphere or co-transported with soil following senescence and decay of the plants is difficult to ascertain at this time. Quite possibly both mechanisms are important: with wind-blown soil being the major source during the drier months, and the direct mechanism contributing significantly at other times of the year.

The higher molecular weight fatty acid salts also show this terrestrial plant wax source, but the fatty acid salt fraction is clearly dominated by the $C_{13}$ - $C_{18}$ fatty acids. As mentioned above, this class of

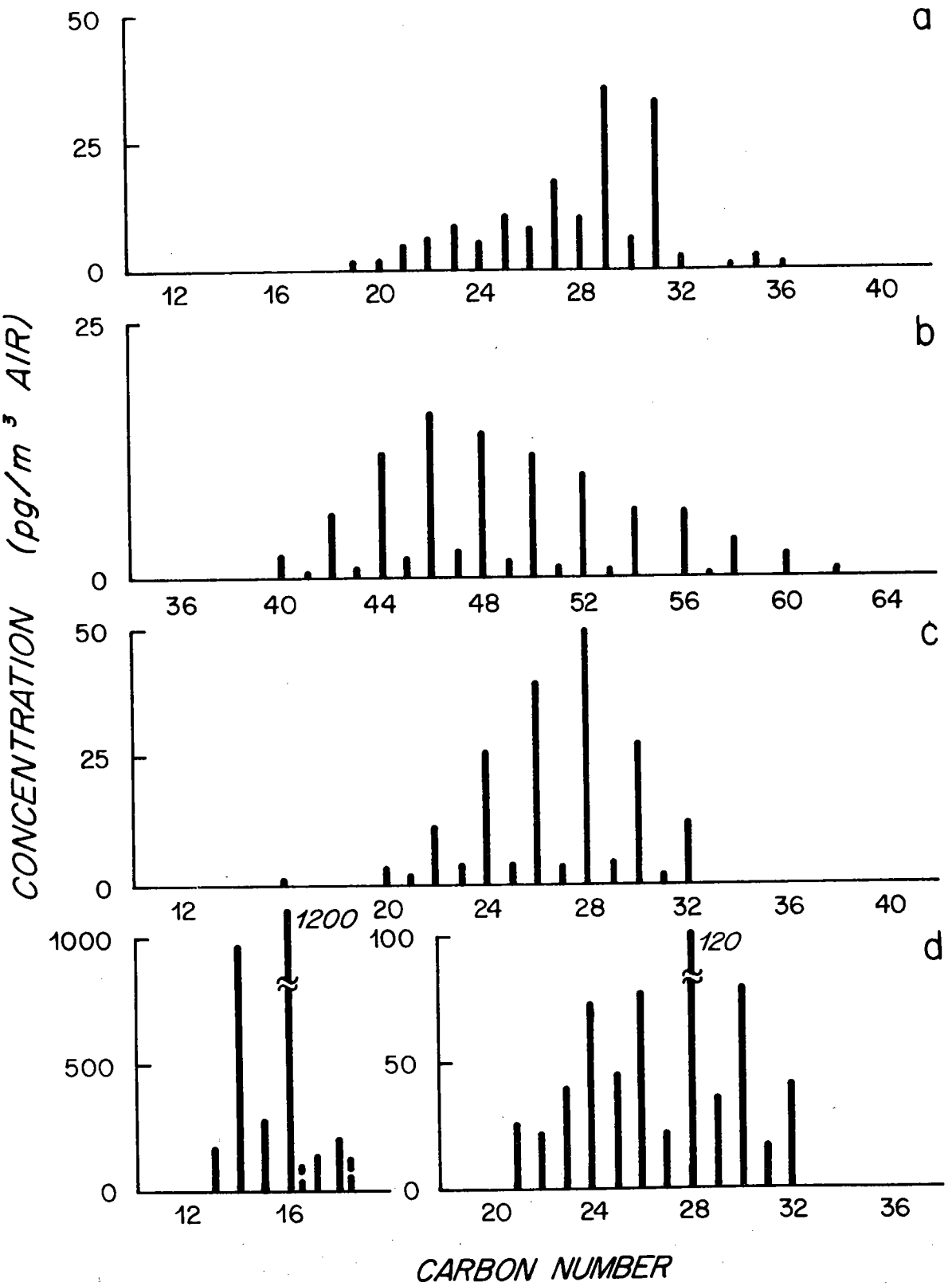


Figure 15 Lipid composition of Enewetak aerosol. (a) n-alkanes, (b) wax estrs, (c) fatty alcohols, (d) fatty acid salts.

compounds may account for as much as 50% of the total extractable organic matter in aerosol samples collected at Enewetak atoll. These fatty acids appear to be of marine origin although they have other sources as well including terrestrial plants and soil [Peltzer and Gagosian, 1983]. The unequivocably marine source polyunsaturated fatty acids were not detected, but these compounds are known to undergo rapid degradation and photo-oxidation. Hence, they would not be expected to survive atmospheric transport or aerosol collection. We attribute a major proportion of the $C_{13}$ to $C_{18}$ fatty acids to a marine source due to their strong correlation with concentrations of Na (from sea-salt); and approximately the same aerosol concentrations of these compounds were observed at Samoa where the terrestrial dust source is much weaker.

The compositions of the fatty alcohol and fatty acids in rain samples collected at Enewetak atoll were found to be very similar to the aerosol compositions. While the fatty alcohols are directly comparable between the two sample types, the fatty acids are not. The fatty acids analyzed in rain are "total" fatty acids. This is due to the fact that the analytical procedure for lipids in rain does not separate the free fatty acid salts as a discrete compound class. Instead, a portion of the rain extract was transesterified yielding the methyl esters of both the free fatty acids and the fatty acids previously esterified as triglycerides, wax and steryl esters, etc. As yet, wax esters have not been analyzed in rain samples since their low concentrations in the aerosols probably means they will be below our detection limits. The hydrocarbons analyzed in the rain samples had a much different composition than in the aerosols. Not only was the n-alkane CPI ~ 1, but there was a large UCM as well.

The mean gas phase composition of n-alkanes is shown in Figure 16 along with the mean aerosol and rain compositions. The gas phase n-alkanes are characterized by concentrations several times higher than the aerosol n-alkanes, a CPI approximately equal to one, and a large UCM. For the limited sample set collected there doesn't appear to be a temporal trend, but any further extrapolation of this data towards a "constant background level of n-alkanes" would be premature. The obvious conclusion that this material represents the unknown source for the CPI = 1 n-alkanes

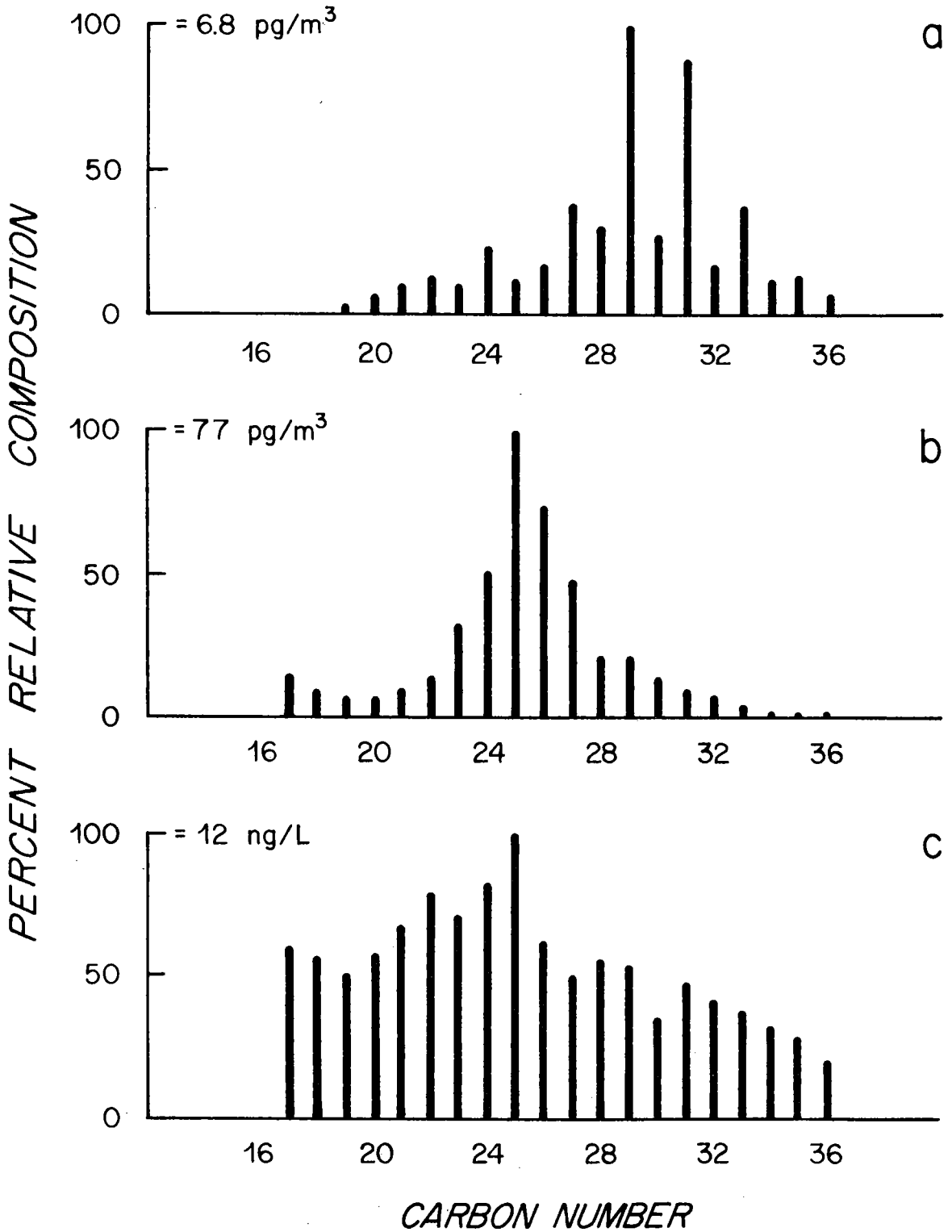


Figure 16 Aerosol, gas phase and rain n-alkane composition at Enewetak atoll. (a) aerosol, (b) gas phase, (c) rain.

in rain is a subject discussed thoroughly elsewhere [Zafiriou et al., 1984].

Sampling artifacts: Like many other analytical methods, this method employs certain procedures which may alter the physical and chemical state of the analyte. In these cases, rather than discard an otherwise acceptable method, it is best to proceed but with full knowledge of the limitations and consequences of the procedure. The collection of atmospheric aerosols on glass fiber filters is one such procedure. The possibilities for altering the physical and chemical state of the analyte are several. First, a filter may not be 100% efficient at collecting the particles of interest. Secondly, a filter may lose components loosely bound to a trapped particle. Thirdly, a filter may adsorb gas phase compounds. And finally, a filter can lose collected material due to secondary interactions. None of these processes are unique to this procedure. Indeed, they are the problems typically associated with the use of filters to collect samples. For our purposes, we accept the GFFs as efficient collectors of atmospheric particulate matter yet realize it is important to emphasize their limitations.

The GFFs are rated as $\geq$ 98% efficient for the collection of particles with radius $\geq$ 0.015 μm [Butcher and Charlson, 1972]. To decide whether single or double GFFs are required for the collection of atmospheric aerosols, two filters were used in series during the Pigeon Key experiment. Typically, double filters have been used by several investigators (for example, see Duce et al. [1983]) for the collection of aerosols. For n-alkanes and fatty alcohols $\geq$ 95% of the material was collected by the first filter. Since these compound classes have the highest vapor pressure of all the compounds we analyzed, we have used single GFFs for the collection of atmospheric aerosols throughout our work.

The second problem in using GFFs for the collection of aerosols deals with the loss of material from the filter. This can result in lower estimates for the "particulate" phase, as well as increased estimates for the gas phase if the gas phase trapping device is installed serially behind the filter. Some of the problems associated with the use of serial particle and gas phase samplers have been discussed by Junk and Jerome

[1983]. Since their ideal solution of a parallel aerosol and gas phase sampler is not available, it is important to remember the potential effects serial sampling can introduce. For example, one of the major processes they cite is the sublimation loss of loosely bound compounds from organic particles and their subsequent trapping by the serially installed gas phase collector. While it is difficult to obtain data that conclusively demonstrates that this process is occurring, it is clear that the potential for this problem exists and it must be considered if the data are to be interpreted in a meaningful way.

The third process affecting the collection of aerosols with GFFs deals with the adsorption of gas phase compounds onto the surface of the filter. For the remote marine locations we sampled, the gas phase concentrations are so low that except for the most reactive of compounds this process is probably negligible. Comparison of our gas phase and aerosol lipid compositions suggests that these are two distinct phases, and adsorption of the gas phase by the GFF is minimal. Indeed, we believe the process proceeds in the other direction based opon our conclusions about hydrocarbons in rain [Zafiriou et al., 1984].

The fourth process affecting the collection of aerosol and gas phase compounds deals with the interaction of trapped compounds with reactive gases in the sampling stream. Not only are compounds lost by this process, but new ones are formed as the product of these reactions. This process is expected to be especially acute for the relatively reactive compounds containing one or more double bonds. Thus, the polyunsaturated fatty acids are especially good candidates for this type of interaction with ozone, hydroxyl radicals, etc. Their absence from the aerosol samples may be evidence for this effect. We have already begun to test this hypothesis by collecting samples only during daylight or night-time hours when the levels of these reactants are significantly different to see if there are any measurable effects of this process. The results of these experiments will be published elsewhere.

A fifth sampling artifact deals solely with the comparison of two different types of aerosol samples. Because of the ability of rain to scavenge aerosols, one might be tempted to consider rain samples as a

different type of "aerosol sample." Indeed, this is exactly what is done whenever a washout ratio (the ratio of the concentration of a particular substance in rain divided by its concentration in air) is calculated. However, there are serious differences between the temporal and spatial sampling characteristics of the two methods that could lead to a misinterpretation of the results. Aerosol samples are typically collected over a period of several days at the base of the marine boundary layer. Rain samples are collected on a discrete event basis lasting from tens of minutes to a few hours in duration while the rain scavenges aerosols from cloud base to ground level. Thus, we are already dealing with two distinctly different "aerosol" samples. An additional factor to be considered is the possibility that gas phase compounds can be adsorbed by the rain drops. Clearly, the comparison of aerosols and rain samples is a very complex situation.

## IV. CONCLUSIONS

We have described a method for the analysis of naturally occurring lipids and waxes in remote marine aerosols. This method is characterized by:

(1) sampling and collection procedures for aerosol, gas phase and rain samples which are essentially free of contamination for the compound classes analyzed;

(2) extraction and silica-gel column chromatography procedures for separating five naturally occurring lipid and wax compound classes (n-alkanes, wax esters, fatty alcohols, sterols and fatty acid salts) and PAHs into discrete compound classes to facilitate identification and quantification of the components;

(3) separation of the fatty acid esters (wax esters, steryl esters, triglycerides, etc.) from the more abundant fatty acid salts since these are different compound classes which represent biologically and geochemically distinct phases, each with its own inherent source marker and transport mechanism information;

(4) HRGC for the identification and quantification of the analytes over a wide range of carbon numbers, i.e. $C_{15}$ - $C_{44}$ for n-alkanes, $C_{39}$ - $C_{62}$ for wax esters and $C_{13}$ - $C_{36}$ for fatty alcohols and fatty acid salts;

(5) procedural and sampling blanks which are sufficiently low to allow detection limits for most compounds on the order of 0.1 - 1.0 $pg/m^3$;

(6) quantitative recoveries and the use of several internal standards which allow for precise quantitation of the analytes; and,

(7) HRGC/MS for the confirmation of compound identifications based on chemical class and GC retention times.

The use of this method for the analysis of compounds in remote marine aerosols has allowed us to:

(1) quantitatively determine the composition of the remote marine aerosol with respect to the lipids and waxes in the five compound classes and PAHs;

(2) identify the major sources of this material to the atmosphere based on the distribution of the major homologs within these five com- pound classes; and,

(3) by combining the rain and dry deposition measurements with the particle size distributions of the compounds (from cascade impactor studies) we have been able to estimate the fluxes of these compounds across the air/sea interface.

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## Appendix

### WHOI/SEAREX LAB PROCEDURES

1. Glassware washing
2. Solvent blanks
3. Glass fiber filter clean-up
4. PUF-plug clean-up
5. Florisil clean-up
6. Glass fiber filter reflux
7. Glass fiber filter acidification and extraction
8. PUF-plug extraction
9. Florisil extraction
10. Rain extraction
11. Silica-gel extraction and deactivation
12. Solvents for silica-gel chromatography
13. Silica-gel chromatography: long-column procedure
14. Fatty alcohol and sterol acetylation
15. Fatty acid methylation
16. Silica-gel chromatography: mini-column procedure

WHOI/SEAREX Lab Procedure #1
Glassware washing

1. While filling enamel basin with hot water, add 2 squirts of conc. liquid micro soap.

2. Put glassware in basin and let soak if necessary.

3. Wash glassware with brushes and avoid handling flask necks and joints with fingers (contamination).

4. Rinse glassware thoroughly with warm tap water.

5. Rinse glassware 3x with distilled water. Use forceps to handle adaptors and small vials.

6. Rinse glassware 3x with acidic methanol (see Tips).

7. Rinse glassware 3x with acetone (500 mL wash bottle).

8. Rinse glassware 3x with methylene chloride (500 mL wash bottle).

9. Place glassware in drying oven at 150°C for ≥ 1 hr.

Tips:

1. Acidic methanol prep. - add 10 mL 2x distilled HCl to 500 mL wash bottle and fill to top with methanol.

2. Run cold water tap while solvent rinsing in sink.

3. Do not discard used solvent in sink. Instead, collect used solvent in a 1-liter Erlenmeyer flask with a large funnel (both preferably teflon or polypropylene so they won't break) when rinsing glassware. Discard used solvent in waste solvent cans for disposal.

4. Do not use acidic methanol when rinsing metal equipment or foil-lined caps.

WHOI/SEAREX Lab Procedure #2
Solvent blanks

1. Measure 200 mL of solvent into a clean 250 mL graduated cylinder. Transfer 177 mL of solvent into a clean 250 mL round-bottom (RB) flask. (Save the rest of the solvent in the graduated cylinder for flask rinses and transfers. See Note 1.) Rota-vap solvent to ~ 5 mL. Recommended water bath temperatures:

| | |
|---|---|
| Methylene chloride | 20°C |
| Hexane, ethyl acetate | 25°C |
| Toluene | 30°C |

   Cooling water temperature for rota-vap @ ~ 5°C.

2. Using a $CH_2Cl_2$ rinsed glass adaptor transfer residue to a $CH_2Cl_2$ rinsed 25 mL pear-shaped (PS) flask with 4 x 5 mL solvent rinses; rota-vap to dryness. (See Note 2.)

3. Using a $CH_2Cl_2$ rinsed pipette, transfer residue to a 2 mL screw-cap (SC) vial with 3 x 1 ml solvent rinses. Evaporate to dryness under a gentle stream of nitrogen at room temp. (use water bath). Watch solvent level closely following last transfer. Shut-off nitrogen and cap vial as soon as all of the solvent evaporates.

4. Label vial and put sample in freezer.

Notes:

1. For ethyl acetate and toluene blanks, transfer all 200 mL to RB-flask. Use clean $CH_2Cl_2$ for rinses and transfers.

2. Do not evaporate hexane or methylene chloride to dryness. Stop rota-vapping @ ~ 1 mL for 25-100 mL PS-flasks, @ ~ 5 mL for larger flasks.

3. If rota-vapping is proceeding very slowly, water bath may be increased ~ 5°C for > 100 mL flasks only.

WHOI/SEAREX Lab Procedure #3
Glass fiber filter clean-up

1. Using $CH_2Cl_2$ rinsed stainless steel (SS) forceps, place five GFFs into a $CH_2Cl_2$ rinsed foil tray. Cover with foil and place in muffle furnace. Set temp. at 450°C and turn on furnace. Combust overnight.

2. Turn furnace off, open doors half-way and allow filters to cool for a few hours. Wear heat-resistant gloves when removing tray of filters from furnace.

3. Using SS forceps, transfer filters from foil tray into giant soxhlet with modified siphon arm (see extraction tip #5). Space filters around walls of soxhlet to avoid bunching.

4. Now set-up 3 soxhlet extraction apparatus in a fume hood. Be sure to allow for easy exchange of the soxhlets. Do not install any soxhlets in the apparatus at this time.

5. Pour 2L of acetone and 2L of methanol into the first 5L RB-flask; add several boiling chips. Now install the soxhlet with GFFs in the first 5-liter flask. Extract the GFFs overnight.

6. Stop acetone/methanol extraction just before the soxhlet cycles. Drain solvent from soxhlet. Add boiling chips and 3.8 L of $CH_2Cl_2$ to the 5L flask next in line. Place soxhlet in the second flask and extract overnight.

7. Stop first $CH_2Cl_2$ extraction just before the soxhlet cycles. Drain solvent from soxhlet. Add boiling chips and 3.8 L of $CH_2Cl_2$ to the 3rd 5L flask. Place soxhlet in the last flask and extract overnight.

8. Stop second $CH_2Cl_2$ extraction and cycle soxhlet. Using SS forceps, transfer filters from soxhlet into a clean 2L beaker. Place beaker in vacuum desiccator and pump down for 6-8 hours.

9. Release vacuum slowly. Using SS forceps, transfer filters from beaker into a clean, one gallon, wide-mouth jar. Cover with foil liner and screw-cap lid. Put teflon tape around the lid and label the jar.

Note:

Clean-up procedure for impactor filters is the same as above except for the following changes:

1. Extract 7 filters at a time.
2. Use an unmodified giant soxhlet.
3. Transfer filters into a 32 oz glass jar before putting into desiccator.

Extraction tips:

1. Re-use 4L of 50/50 acetone/methanol 4 times.
2. Re-use $CH_2Cl_2$ from second $CH_2Cl_2$ extraction of one GFF lot for first $CH_2Cl_2$ extraction of next lot of GFFs.
3. Use only fresh solvent for the second (final) $CH_2Cl_2$ extraction.
4. Alternate extracting 8 x 10 GFFs and ICSs so time is not lost cleaning soxhlets for that day's extractions.
5. The modified soxhlet consists of a standard 100 mm ID x 300 mm long soxhlet with the siphon-tube extended so that the GFFs are completely immersed in solvent before the soxhlet cycles.
6. Do not alternate PUF-plugs with GFFs. To avoid contamination, extract the GFFs first then the PUF-plugs. Never re-use $CH_2Cl_2$ from a PUF-plug extraction to extract GFFs.

WHOI/SEAREX Lab Procedure #4
Polyurethane-foam plug clean-up

1. Place a PUF-plug in a 600 mL beaker and rinse with water until sudsing stops. (Use the base of a 100 mL grad. cylinder to compress plug inside beaker. Repeat several times to rinse plug.)

2 Using base of cylinder, squeeze excess water from plug. Transfer plug to a 1L beaker containing a 1:1 acetone/methanol mixture (400 mL each; see note) and rinse plug to remove water.

3. Set-up 3 soxhlet extraction apparatus as in WHOI/SEAREX Lab Procedure #3 (LP-3): Glass fiber filter clean-up.

4. Using base of cylinder, squeeze remaining solvent from plug. Using SS forceps, transfer plug to clean soxhlet (100 mm ID x 300 mm long). Add boiling chips to 5L RB-flask containing 1:1 acetone/methanol mixture (2L each; see note). Place soxhlet in flask and extract overnight.

5. Stop extraction; cycle soxhlet. Carefully tip apparatus in direction of siphon to start solvent draining into flask.

6. Add boiling chips and 3.8L of $CH_2Cl_2$ to 5L RB-flask next in line. Place soxhlet in flask and extract overnight.

7. Repeat steps #5 and #6 using clean $CH_2Cl_2$.

8. Repeat Step #5. Using SS forceps remove plug slowly from soxhlet. Stop withdrawing PUF-plug near top of soxhlet and let solvent drain. Use forceps to gently squeeze plug against inside of soxhlet to expel excess solvent. Place plug in vacuum desiccator in upright position. Pump down for about 12 hours, or until PUF-plug is "dry".

9. Release vacuum slowly. Using SS forceps, place plug in a 32 oz glass jar and cover with foil and a foil-lined screw cap. Seal cap with teflon tape, label, store in cool dark place.

Notes:

1. The 1:1 acetone/methanol mixture should not be used for more than 4 plug extractions.
2. Re-use the solvent from the second $CH_2Cl_2$ extraction for the first $CH_2Cl_2$ extraction.
3. Use only fresh solvent for the final $CH_2Cl_2$ extraction.
4. Remember to rinse the outside of the graduated cylinder with $CH_2Cl_2$ before using to compress PUF-plug to expel excess solvent.

WHOI/SEAREX Lab Procedure #5
Florisil clean-up

1. Transfer 1200 cc of florisil (16/30 mesh) to a clean 2L beaker. Add $CH_2Cl_2$ to ~ 1800 mL, then stir vigirously with a glass rod to slurry mixture. Let settle 5 min and decant $CH_2Cl_2$.

2. Add more $CH_2Cl_2$ to 1800 mL, slurry, let settle 5 mins and decant $CH_2Cl_2$.

3. Repeat step 2 one more time.

4. Transfer florisil to SS-pan (195 x 315 x 55 mm). Spread-out with glass rod to form a quasi-uniform layer of florisil. Do not pack down; try to fluff-up florisil with the glass rod.

5. Cover pan with solvent rinsed aluminum foil.

6. Oven dry @ 120°C for 1-2 hours. Stir occasionally. Watch-out for solvent fumes.

7. Transfer pan to muffle furnace (furnace off or just slightly warm), then heat tO 450°C for 20 hours (including warm-up time).

8. Shut-off muffle furnace. Let cool 1-2 hours with door 1/2 open.

9. Remove pan from muffle furnace. Let cool 1 hour in oven @ 120°C.

10. Transfer florisil to pyrex crystallizing dish (190 x 100 mm) and place in vacuum desiccator. Evacuate desiccator with water aspirator for 15-20 mins then seal and let stand overnight.

11. Sub-divide lot into 8-45 gm portions and transfer each to an 8 oz glass jar with aluminum foil lined cap. Seal jar with 1" wide teflon tape.

12. Store jars @ room temperature prior to sampling.

WHOI/SEAREX Lab Procedure #6
Glass fiber filter reflux

1. Thoroughly defrost frozen sample.

2. Rinse 1L RB-flask with $CH_2Cl_2$; add ∿ 4 $CH_2Cl_2$ extracted boiling chips and rinse 2x more. Cover flask with foil.

3. Using large pair of $CH_2Cl_2$ rinsed SS forceps, remove GFF from sample jar and place on $CH_2Cl_2$ rinsed foil boat.

4. Using 2 pair of large SS forceps tear up GFF into small pieces and transfer to 1L flask.

5. Add 400 mL $CH_2Cl_2$ to flask. Using syringe add internal standard mixture of recovery standards to flask (see Tips).

6. Reflux overnight.

7. Stop refluxing and let solution cool.

8. Filter sample through $CH_2Cl_2$ rinsed glass frit funnel (25-50 μm) and collect filtrate in 1L RB-flask.

9. Rinse filter pieces with 4 x 50 mL $CH_2Cl_2$ and filter each rinse the same as in Step #8.

10. Stopper flask containing filter pieces, wire shut and refrigerate. Save flask and filter pieces for acidic methanol/hexane extraction (LP-7: GFF acidification and extraction).

11. Rota-vap filtrate down to ∿ 5 mL at 20°C in 1L RB-flask.

12. Transfer to 50 mL PS-flask with 4 x 10 mL $CH_2Cl_2$ rinses. Rota-vap to ∿ 1 mL @ 20°C.

13. Transfer to 2 mL SC-vial with 3 x 1 mL $CH_2Cl_2$ rinses.

14. Cap vial, label and freeze.

Tips:

When using syringes be sure to pull a solvent plug (∿ 1-2 μL) and an air plug (∿ 1-2 μL) before measuring amount of standard in syringe barrel.

WHOI/SEAREX Lab Procedure #7
Glass fiber filter acidification and extraction

1. Remove flask containing filter pieces from refrigerator and allow to warm up to ambient.

2. Add 100 mL of 0.1 M HCl/methanol to filter pieces. Using same graduated cylinder measure 100 mL hexane and add to filter pieces.

3. Add standard to mixture and stopper flask. Mix contents thoroughly venting stopper occasionally to release solvent vapors.

4. Filter solution through a hexane rinsed glass frit funnel (25-50 μm) and collect filtrate in a $CH_2Cl_2$ rinsed 250 mL RB-flask.

5. Transfer filtrate to $CH_2Cl_2$ rinsed 250 mL separatory funnel. Shake funnel vigorously, then let phases separate.

6. Transfer lower layer from separatory funnel back into flask containing filter pieces.

7. Drain hexane from separatory funnel into $CH_2Cl_2$ rinsed 500 mL RB-flask.

8. Add 50 mL hexane to filter pieces, stopper flask and shake vigorously.

9. Repeat steps #4 - #7.

10. Repeat steps #8 and #9. NOTE: Total volume of hexane used for extraction = 200 mL.

11. Rota-vap hexane in 500 mL RB-flask to ∿ 5 mL dryness @ 25°C.

12. Transfer to 25 mL PS-flask with 4 x 5 mL hexane rinses. Rota-vap to ∿ 1 mL @ 25°C.

13. Transfer to a 2 mL SC-vial with 3 x 1 mL hexane rinses. Evaporate to dryness under nitrogen @ room temperature.

14. Cap vial, label and freeze.

Preparation of 0.1 M HCl/methanol:

1. Prepare 2 clean 1L separatory funnels and 1 pt brown glass SC-bottle.

2. Into separatory funnel #1 add:
   250 mL methanol
   250 mL permanganate distilled water
   10 mL 6 M doubly distilled HCl
   100 mL hexane

3. Shake mixture vigorously, let phases separate, then drain-off lower layer into separatory funnel #2. DO NOT transfer meniscus to sep. funnel #2.

4. Add 100 mL hexane to separatory funnel #2, shake vigorously, then let phases separate.

5. Drain hexane layer from separatory funnel #1 and discard. Rinse funnel 3x with hexane.

6. Transfer lower layer from separatory funnel #2 into separatory funnel #1. Add 100 mL hexane to separatory funnel #1, shake vigorously, then let phases separate.

7. Drain hexane layer from separatory funnel #2 and discard. Rinse funnel 3x with hexane.

8. Transfer lower layer from separatory funnel #1 into separatory funnel #2. Add 100 mL hexane to separatory funnel #2, shake vigorously, then let phases separate.

9. Drain lower layer from separatory funnel #2 into a clean brown glass bottle. Cap and seal with teflon tape.

10. Label: 0.1 M HCl/methanol
    4x Hexane extracted
    Date

WHOI/SEAREX Lab Procedure #8
Polyurethane foam plug extraction

1. Remove PUF-plug from freezer and allow it to warm-up to ambient before opening jar. This prevents condensation from forming on the plug which may contaminate the sample.

2. Rinse a 5L RB-flask 3x with $CH_2Cl_2$, fill with 3.0L $CH_2Cl_2$, add 6-8 boiling stones then stopper flask.

3. Rinse down inside of condenser and outside of bottom joint with $CH_2Cl_2$. Position in hood sufficiently above the bench top to allow for installation of the 5L flask and the soxhlet.

4. Place 5L flask in a heating mantle in the hood.

5. Rinse soxhlet (100 mm ID x 300 mm long) with $CH_2Cl_2$, then lay-down on its side on the bench. Carefully remove PUF-plug from glass jar with giant size forceps and immediately place inside soxhlet.

6. Apply internal standard solution containing recovery standards directly to PUF-plug with an 11.0 cm needle microliter syringe.

7. Assemble soxhlet apparatus in hood. Check to see that drying tube at top is correctly positioned and desiccant is not exhausted.

8. Start solvent refluxing. Note time solvent first starts condensing and draining into soxhlet.

9. Turn-off heating mantle approx. 20 hours later. Try to turn-off heating mantle so that soxhlet has almost finished filling and does not cycle.

10. Carefully raise condenser to separate from soxhlet. Cycle soxhlet and drain solvent into 5L flask by tipping assembly slowly towards side with siphon. Let solvent drain into flask.

11. Carefully remove PUF-plug from soxhlet with giant size forceps. Let excess $CH_2Cl_2$ drain into soxhlet, then place plug in hood to air dry. (Discard when dry - do not re-use.) Tip soxhlet so last mL of $CH_2Cl_2$ drain into 5L flask, then remove soxhlet from flask.

12. Transfer $CH_2Cl_2$ to a 1L RB-flask in 3 or 4 equal portions and rota-vap to $\sim$ 5 mL @ 20°C. Transfer residual solution to a 50 mL PS-flask with 4 x 10 mL $CH_2Cl_2$ rinses and rota-vap to $\sim$ 0.5 - 1.0 mL @ 20°C.

13. Transfer residual solution to a 2 mL SC-vial with 3 $\sim$ 0.5 mL $CH_2Cl_2$ rinses and evaporate to dryness under nitrogen at room temperature.

14. Label vial and store in freezer.

WHOI/SEAREX Lab Procedure #9
Florisil extraction

1. Remove florisil sample from freezer and allow it to warm-up to ambient before opening jar. This prevents condensation from forming on the florisil which may contaminate the sample.

2. Rinse a 1L RB-flask 3x with $CH_2Cl_2$, fill with 500 mL $CH_2Cl_2$, add 4-6 boiling stones then stopper flask.

3. Rinse down inside of condenser and outside of bottom joint with $CH_2Cl_2$. Position in hood sufficiently above the bench top to allow for installation of the 1L flask and the soxhlet.

4. Place 1L flask in a heating mantle in the hood.

5. Rinse soxhlet (50 mm ID x 200 mm long) with $CH_2Cl_2$, then lay-down on side on bench. Place pre-extracted cellulose thimble (43 mm OD x 123 mm long, single thickness) upright in a 250 mL beaker. Carefully transfer florisil to thimble using giant size forceps.

6. Apply internal standard solution containing recovery standards directly to florisil with an 11.0 cm needle microliter syringe.

7. Place thimble in soxhlet, then assemble soxhlet apparatus in hood. Check to see that drying tube at top is correctly positioned and desiccant is not exhausted.

8. Start solvent refluxing. Note time solvent first starts condensing and draining into soxhlet.

9. Turn-off heating mantle approx. 20 hours later. Try to turn-off heating mantle so that soxhlet has almost finished filling and does not cycle.

10. Carefully raise condenser to separate from soxhlet. Cycle soxhlet and drain solvent into 1L flask by tipping assembly slowly towards side with siphon. Let solvent drain into flask.

11. Carefully remove thimble from soxhlet with giant size forceps. Let excess $CH_2Cl_2$ drain into soxhlet, place thimble in glass jar (32 oz, tall form) temporarily, then slowly tip soxhlet so last mL of $CH_2Cl_2$ drain into 1L flask. Remove soxhlet from flask.

12. Transfer extract to 1L RB-flask taking care not to transfer boiling stones. Rinse extraction flask 2x with 25 mL portions of $CH_2Cl_2$ and combine with extract. Rota-vap to $\sim$ 5 mL @ 20°C. Transfer residual solution to a 50 mL PS-flask with 4 x 10 mL $CH_2Cl_2$ rinses and rota-vap to $\sim$ 0.5 - 1.0 mL @ 20°C.

13. Transfer residual solution to a 2 mL SC-vial with 3 x 0.5 mL $CH_2Cl_2$ rinses and evaporate to dryness under nitrogen at room temperature.

14. Label vial and store in freezer.

15. Dump out and discard florisil. Place thimble in glass jar and vacuum desiccate until extraction thimble is dry. Save thimble for re-use.

WHOI/SEAREX Lab Procedure #10
Rain extraction

Part I. Field work-up:

1. Immediately after the rain stops, cover the rain bowl, remove the 5L flask from rain collector, stopper flask, and return sample to the lab. Record time and net rainfall (inches).

2. Sub-divide sample for TOC, nutrient and anion/cation analyses. Record volume used for each.

3. Estimate volume of rain remaining in 5L flask.

4. Add internal standard solution containing recovery standards and acidify sample as follows:
   a) 10 µL internal standard solution/1-3L sample, or
      20 µL internal standard solution/3-5L sample.
   b) 1 mL 6 M doubly distilled HCl/500 mL rain.

5. Transfer rain sample to a clean 3L separatory funnel (total sample if volume ≤ 2.5L, 1/2 sample if volume > 2.5L), then extract 4x with 100 mL aliquots of $CH_2Cl_2$. Collect $CH_2Cl_2$ extracts in brown glass bottle. Seal bottle with teflon tape, label and store @ -10°C.

6. Measure and record extracted rain volume.

7. Repeat extraction with second half of sample, if sample was split. Use the same separatory funnel as for the first half of the sample, but collect $CH_2Cl_2$ extracts in a second brown glass bottle.

8. Samples need not remain frozen during shipment, but should be stored in freezer immediately upon arrival @ WHOI.

Part II. Laboratory work-up:

1. Thaw sample for a few hours, then transfer to a 500 mL RB-flask (in several portions if volume is ≥ 300 mL) and rota-vap to ~ 2 mL @ 20°C. Transfer residual solution to a large centrifuge tube (27 x 100 mm) then rinse flask 3x with 3.3 mL aliquots of hexane and combine with residual solution in centrifuge tube.

2. Rinse sample bottle with 3.3 mL 0.1 M HCl/methanol, transfer to 500 mL RB-flask, rinse, then add to centrifuge tube.

3. Repeat bottle and flask rinse 2x more with 3.3 mL aliquots of 0.1 M HCl/methanol. Combine rinses in centrifuge tube. Cap tube with teflon lined screw-cap.

4. Vigorously shake mixture, then centrifuge to separate layers. Draw-off hexane layer with pipette and transfer to a 100 mL PS-flask.

5. Repeat extraction 3x more with 10 mL aliquots of hexane; combine each in PS-flask with initial extract.

6. Rota-vap extract @ 25°C to near dryness.

7. Transfer residue to a 2 mL SC-vial: Rinse flask 3x with 0.5 mL portions of hexane and transfer to vial. Evaporate solution to dryness with nitrogen @ room temperature.

8. Label flask and store in freezer.

Notes:

1. Nominal composition of internal standard solution:
   10 ng/µL a-$C_{24}$ 3-methyltricosane
   10 ng/µL FLU-$d_{10}$ fluorene-$d_{10}$
   10 ng/µL p-TPH-$d_{14}$ p-terphenyl-$d_{14}$
   10 ng/µL $W_{41}$ nonadecyl docosanoate
   10 ng/µL n-$O_{17}$ n-heptadecan-1-ol
   40 ng/µL a-$S_{19}$ 16-methyloctadecanoic acid
2. Prepare 0.1 M HCl/methanol as per method described in LP-7: GFF acidification and extraction.

WHOI/SEAREX Lab Procedure #11
Silica-gel extraction and deactivation

1. Using top loading balance, weigh out 125 gms silica-gel (Bio-Sil A 100-200 mesh) into a clean 400 mL beaker.

2. Transfer silica-gel into a $CH_2Cl_2$ extracted cellulose thimble - Whatman, 60 mm OD x 160 mm long. (Trim 20 mm from a 60 mm OD x 180 mm long thimble using scissors prior to $CH_2Cl_2$ extraction.)

3. Using stainless steel forceps, place thimble in clean extractor with modified siphon arm (see Note #2). Fill 3L RB-flask about 1/2 full with $CH_2Cl_2$ and add boiling chips.

4. Extract overnight.

5. Stop extracting and let soxhlet drain. Using SS forceps, place thimble in a tall, wide mouth jar and cover loosely with foil. Leave jar in fume hood for $\sim$ 6 hours.

6. Handling thimble with forceps, transfer silica-gel into clean SS tray and cover loosely with $CH_2Cl_2$ rinsed foil. Bake in pre-heated oven at 225°C for $\sim$ 64 hours.

7. Remove silica-gel from oven and carefully but quickly transfer to a clean 16 oz glass jar. Put jar in desiccator and pump down for about a half-hour and retain vacuum.

8. When completely cooled, slowly release vacuum. Transfer activated silica-gel to a pre-weighed clean and dry glass bottle with stopper (see Note #3). Weigh stoppered bottle containing silica-gel. Determine silica-gel weight.

9. Deactivate silica-gel by adding 5% of its weight of permanganate-distilled water (PD-$H_2O$) i.e., 5 mL per 100 g of silica-gel. Using a long pipette, add water dropwise in 0.5 mL portions. After each 0.5 mL, stopper bottle and shake until clumps disappear. Seal stopper with teflon tape.

10. Let deactivated silica-gel sit three days (shaking occasionally) before using.

NOTES:
1. The overall procedure requires $\sim$ 1 week (2 days in oven). To save time, start the extraction on a Thursday so that silica-gel can dry in oven over the weekend.

2. The modified soxhlet consists of a standard 70 mm ID x 235 mm long soxhlet with the siphon-tube extended so that the thimble is completely immersed in solvent before the soxhlet cycles.

3. The bottle for storing the deactivated silica-gel must have a tight fitting stopper. It is preferable to use a glass bottle whose stopper has been hand-lapped for a perfect fit.

WHOI/SEAREX Lab Procedure #12
Solvents for silica-gel chromatography

A. Necessary glassware
1. 10 pint size brown bottles with 10 foil-lined caps and teflon liners.
2. 500 mL graduated cylinder for measuring toluene and hexane.
3. 100 mL graduated cylinder for measuring ethyl acetate.

B. Necessary solvents
1. Toluene
2. Ethyl acetate
3. Hexane

C. Solvent Recipes

| | | |
|---|---|---|
| 1. | Hexane | 400 mL |
| 2. | 25% toluene | 100 mL |
| | 75% hexane | 300 mL |
| 3. | 50% toluene | 200 mL |
| | 50% hexane | 200 mL |
| 4. | 5% ethyl acetate | 20 mL |
| | 95% hexane | 380 mL |
| 5. | 10% ethyl acetate | 40 mL |
| | 90% hexane | 360 mL |
| 6. | 15% ethyl acetate | 60 mL |
| | 85% hexane | 340 mL |
| 7. | 20% ethyl acetate | 80 mL |
| | 80% hexane | 320 mL |
| 8. | Ethyl acetate | 400 mL |
| 9. | Methanol | 400 mL |
| 10. | Permanganate distilled water | 400 mL |

D. Procedure
1. Measure-out first solvent required and add to bottle.
2. Measure-out second solvent required and add to bottle.
3. Cap bottle and shake well. Label bottle.
4. To save repetitive rinsing of 500 mL graduate when first preparing all 10 solvents, measure-out toluene for bottles 2 and 3 then rinse graduate with hexane and proceed with solvent preparations.

WHOI/SEAREX Lab Procedure #13
Silica-gel chromatography: long-column procedure

A. NECESSARY GLASSWARE

1. Column (9 mm ID x 300 mm with 250 mL bulb)
2. 20 mL beaker
3. 250 mL Erlenmeyer flask
4. 25 mL and 50 mL graduated cylinders
5. 5-50 mL and 2-100 mL PS-flasks
6. Long tipped 2 ml pipette and rubber bulb
7. Acidic-methanol wash bottle
8. Acetone wash bottle
9. Methylene chloride wash bottle
10. Hexane wash bottle

B. COLUMN PREPARATION

1. Fill column to base of bulb with PD-$H_2O$.
2. Cut small piece of glass wool and place in opening of column with forceps.
3. Tamp glass wool down column using long glass rod and press into place (tamp lightly).
4. Drain $H_2O$ to just above glass wool.
5. Rinse column 3x each with acidic methanol, acetone, methylene chloride and hexane.
6. Fill column to base of bulb with hexane.
7. Weigh 7 gm of silica-gel (5% deactivated, see LP-11: Silica-gel extraction and deactivation) into 100 mL beaker.
8. Add hexane to 40 mL level; then slurry.
9. Try to pour most of slurry into column on first try.
10. Let silica-gel settle momentarily, then begin draining column; tap sides of bulb to make silica-gel fall into column.
11. Rinse beaker walls with hexane to transfer remaining silica-gel; or, if small quantity, let solvent evaporate by holding beaker horizontal, then gently tap beaker to loosen silica-gel and transfer to column as a free flowing powder.
12. Tap side of column 2 or 3 times (up and down) to facilitate settling of silica-gel.
13. Close stopcock when hexane level is just above silica-gel. Tap bulb to free silica-gel sticking on sides.
14. Rinse to base of bulb with short squirts of hexane to wash loose silica-gel into column.
15. Rinse graduated cylinders with methylene chloride and hexane.
16. Rinse pipette with methylene chloride and hexane.
17. Fill graduated cylinder with more than 50 mL hexane and use extra to rinse pipette.
18. Rinse opening of bulb very slowly to cover all sides of bulb. Drain.
19. Repeat rinse and slowly pour remainder of hexane into column rinsing all sides.
20. Drain; rinse column tip with hexane shortly before hexane level in column reaches silica-gel.

C. LOADING SAMPLE

1. Place collecting flask ($CH_2Cl_2$ rinsed) under column.
2. Fill small cylinder with 21-22 mL hexane. Rinse pipette with excess and bring solvent level to 20 mL with pipette.
3. Take 1/4 mL up in pipette and transfer to sample vial, hold vial @ 45° angle and rotate between fingers to dissolve sample.
4. Transfer sample to column by carefully touching pipette to inside of column. Dispense slowly. Drain solvent from column. Repeat twice more.
5. Bring solvent level in graduate to 19 mL with pipette (take-up ~ 1/4 mL) and use to rinse neck of column. Drain column.
6. Add 1 mL of hexane by rinsing opening of bulb. Drain column.
7. Repeat but don't drain, add remaining solvent in cylinder. Drain column so that the solvent level is just above the silica gel.
8. Remove fraction and stopper flask; put new sample flask in place.
9. Continue eluting column with next solvent.

D. COLUMN ELUTION SCHEDULE (SX/SGC-3)

| Fraction | Volume | Solvent | Compound classes |
|---|---|---|---|
| L1 | 20 mL | Hexane | Sat'd. alkanes → dienes |
| L2 | 10 mL | Hexane | PAHs |
| | 20 mL | 25% Tol/Hex | |
| L3 | 20 mL | 50% Tol/Hex | Wax and steryl esters |
| L4 | 20 mL | 5% EtOAc/Hex | Triglycerides, steroid |
| | 20 mL | 10% EtOAc/Hex | ketones |
| L5 | 20 mL | 15% EtOAc/Hex | Fatty alcohols |
| L6 | 20 mL | 20% EtOAc/Hex | Sterols |
| L7 | 30 mL | Ethyl acetate | "polar lipids" |
| | 30 mL | Methanol | |

E. ELUTION TIPS

1. Always add excess solvent to graduated cylinder, then use pipette to adjust to proper level. This rinses pipette with solvent.
2. Always change flask for new fraction before adding solvent to column.
3. Always rinse column reservoir with 1 mL of new solvent, drain, and rinse with 2nd mL of new solvent before adding bulk of new solvent to the column. This insures sharp transitions between solvents and reproducible elution patterns.
4. For methylated/transesterified samples, fractions L3 and L4 are collected together and designated L3 + L4. No wax esters and/or triglycerides will be present - only FAMEs.
5. Rota-vap L1 to near-dryness, then transfer to 2 mL SC-vial with hexane. Rota-vap all other fractions to dryness, then transfer each to a 2 mL SC-vial with 3 x 1 mL hexane rinses. Store all fractions in freezer.

WHOI/SEAREX Lab Procedure #14
Fatty alcohol and sterol acetylation

1. The sample (generally fractions L4 and/or L5 containing ≤ 100 µg fatty alcohols and/or sterols) is transferred to a 2 mL SC-vial with 3 or 4 1 mL hexane rinses and is evaporated to dryness with a gentle stream of nitrogen at room temperature (water bath).

2. Add 35 µL hexane to vial and mix carefully.

3. Add 10 µL pyridine (reagent grade) to vial.

4. Add 10 µL acetic anhydride (reagent grade) to vial and mix thoroughly on vortex mixer for ∿ 1 minute.

5. Let stand overnight in the hood.

6. Add ∿ 0.5 mL hexane to vial and mix. Solution should be clear and not separate into two layers. If not, add more (∿ 0.1 mL) hexane.

7. Add 250 µL 3 M HCl (3x hexane extracted) to vial and shake vigorously. Let stand to separate layers.

8. Remove upper layer (hexane) with pasteur pipette and transfer to a clean 2 mL SC-vial.

9. Repeat extraction twice more with 0.5 mL aliquots of hexane. Combine extracts in 2 mL SC-vial.

10. Evaporate solution to dryness with a gentle stream of nitrogen at room temperature (water bath).

11. GC sample directly (splitless injection only) or clean-up derivatives with mini-column (preferred for on-column injection). See LP-16: Silica-gel chromatography: mini-column procedure.

12. Store sample in freezer.

Preparation of 3 M HCl:

1. Prepare 2 clean 1L separatory funnels and 2 clean 100 mL SC-bottles.

2. Into separatory funnel #1 add:

   100 mL permanganate distilled water
   100 mL 6 M doubly distilled HCl
    50 mL hexane

3. Shake mixture vigorously, let phases separate, then drain-off lower layer into separatory funnel #2. Do not allow meniscus to pass through into separatory funnel #2.

4. Add 50 mL hexane to separatory funnel #2, shake vigorously, then let phases separate.

5. Drain hexane layer from separatory funnel #1 and discard. Rinse funnel 3x with hexane.

6. Transfer lower layer from separatory funnel #2 into separatory funnel #1. Add 50 mL hexane and shake vigorously. Let phases separate.

7. Drain lower layer from separatory funnel #1 into clean bottles. Cap and seal with teflon tape.

8. Label: 3 M HCl
   3x Hexane extracted
   Date

WHOI/SEAREX Lab Procedure #15
Fatty acid methylation

1. Prepare ∿ 3% $BF_3/CH_3OH$ by extracting 14% $BF_3/CH_3OH$ 3x with equivalent volumes of hexane - let stand in freezer to separate layers - then dilute to 1/5 concentration. Store extracted concentrate and diluted reagent in freezer.

2. The sample (containing ≤ 100 µg fatty acids) is transferred quantitatively to a micro-reaction tube (2 mm ID x 100 mm) with 3 x 100 µL of hexane. The solution is evaporated to near dryness with a gentle stream of nitrogen at room temperature after each transfer, and to full dryness after the last transfer.

3. Add 100 µL of ∿ 3% $BF_3/CH_3OH$ to the micro-tube, purge micro-tube for ∿ 2 minutes with nitrogen to expel all air, then seal tube with a flame. Be careful not to pyrolyze solvent or sample - inside walls of tube where you seal must not be wet with solvent or reagent.

4. Heat reaction mixture @ 100°C (boiling water bath) for 30 mins.

5. Stop reaction by plunging mixture into ice/methanol bath.

6. After opening micro-tube, transfer reaction mixture quantitatively to a 16 x 100 mm SC-culture tube by rinsing 3x with 100 µL methanol then 3x with 100 µL hexane. Add ∿ 1-2 mL hexane then ∿ 1-2 mL sat'd NaCl solution (pre-extracted 3x with hexane). Mix vigorously then centrifuge to separate layers. Draw-off top layer (hexane) with a pasteur-pipette and transfer to a 25 mL PS-flask.

7. Repeat extraction 2x more with ∿ 1-2 mL hexane per each. Combine hexane extracts in 25 mL PS-flask.

8. Rota-vap hexane solution to near dryness @ ≤ 25°C, then transfer residue to a 2 mL SC-vial with 3 x 1 mL hexane rinses. Evaporate to dryness under nitrogen at room temperature.

9. GC sample directly (splitless injection only) or clean-up derivatives with mini-column (preferred for on-column injection). See LP-16: Silica-gel chromatography: mini-column procedure.

10. Store sample in freezer.

WHOI/SEAREX Lab Procedure #16
Silica-gel chromatography: mini-column procedure

A. NECESSARY GLASSWARE AND REAGENTS

1. Silica-gel as prepared according to LP-11.
2. Elution solvents are prepared according to LP-12.
3. Column: 125 mm x 6 mm ID with solvent reservoir and luer tip.
4. Stopcock: Hamilton miniature inert valve M/N 1FM1.
5. Column cover: 50 mm dia. petri-dish bottom.
6. 25 mL PS-flasks (several).
7. 10 mL graduated cylinder.
8. Long-tipped pasteur pipette with rubber bulb.
9. Acidic methanol wash bottle.
10. Acetone wash bottle.
11. Methylene chloride wash bottle.
12. Hexane wash bottle.

B. COLUMN PREPARATION

1. Set-up mini-column and attach mini-valve to bottom. Fill column to base of reservoir with PD-$H_2O$ and insert glass wool plug using a long-tip pasteur pipette. Drain $H_2O$ to just above glass wool.
2. Rinse column 3x with acidic methanol, acetone, methylene chloride and hexane.
3. Fill column to base of reservoir with hexane.
4. Weigh 1.00 gm 5% deactivated silica-gel into a 25 mL beaker. Slurry with ~10 mL hexane.
5. Try to pour most of silica-gel into column on first try.
6. Let silica-gel settle momentarily, then begin draining column.
7. Rinse beaker with hexane to transfer remaining silica-gel; or, if small quantity, let solvent evaporate by holding beaker horizontal, then gently tap beaker to loosen silica-gel and transfer as a free-flowing powder.
8. Tap sides of bulb to facilitate settling of silica-gel into column.
9. Tap sides of column (bottom to top) to facilitate uniform packing of column.
10. Close stopcock when hexane level is just above silica-gel. Tap bulb to free silica-gel sticking to sides. Rinse bulb with hexane to wash remaining silica-gel into column. Drain hexane from column as before: stopping when solvent level is just above silica-gel.
11. Rinse 10 mL graduated cylinder with methylene chloride and hexane.
12. Rinse pipette with same.
13. Fill graduated cylinder with 11-12 mL hexane; use excess of 10 mL to rinse pipette.
14. Rinse column reservoir with 0.5 mL hexane.
15. Repeat rinse of reservoir then slowly add rest of hexane. Drain column until solvent level is just above silica-gel; towards end of solvent, rinse stopcock tip with hexane.

C. LOADING SAMPLE

1. Place collecting flask ($CH_2Cl_2$ rinsed) under column.
2. Fill graduated cylinder with 11-12 mL hexane; use pipette to bring level to 10 mL and discard excess solvent after rinsing pipette.
3. Take-up 1/4 mL hexane in pipette and transfer to sample vial. Hold vial @ $\sim 45°$ angle and rotate between fingers to dissolve residue.
4. Transfer to column with pipette by carefully touching pipette tip to inside of column $\sim$ 1 cm above silica-gel. Dispense slowly. Drain and collect solvent. Repeat twice more.
5. Take-up 4th 1/4 mL of hexane and rinse neck of column. Drain and collect solvent.
6. Take-up 1/2 mL hexane, rinse down column reservoir, drain and collect solvent.
7. Take-up 1/2 mL hexane, rinse down column reservoir but do not drain. Add remaining hexane in graduated cylinder. Drain column until solvent level is just above silica-gel.
8. Remove fraction and stopper flask; put new sample flask in place.
9. Proceed with column elution schedule.

D. COLUMN ELUTION SCHEDULE

| Fraction | Volume | Solvent | Compound classes |
|---|---|---|---|
| M1 | 10 mL | Hexane | Hydrocarbons |
| M2 | 5 mL | 25% Tol/Hex | -- |
| M3 | 5 mL | 5% EtOAc/Hex | Alcohols acetates; FAMEs |
| M4 | 5 mL | 10% EtOAc/Hex | |
| M5 | 5 mL | 15% EtOAc/Hex | Fatty alcohols and sterols |
| M6 | 5 mL | 20% EtOAc/Hex | Fatty alcohols and sterols |

E. ELUTION TIPS

1. Always add excess solvent to graduated cylinder then use pipette to adjust to proper level. This rinses pipette with solvent.
2. Always change flask for new fraction before adding solvent to column.
3. Always rinse column reservoir with 1/2 mL of new solvent, drain, and rinse with 2nd 1/2 mL of new solvent before adding bulk of new solvent to the column. This insures sharp transitions between solvents and reproducible elution patterns.
4. For derivative clean-up: fractions M1 and M2 are collected together, then discarded. Fraction M3 containing fatty alcohol/sterol acetates or fatty acid methyl esters is collected and saved. Fractions M4, M5 and M6 are generally omitted. Fraction M3 solvent volume may also be increased to 7 mL.

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Edward T. Peltzer, Jane B. Alford and Robert B. Gagosian

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**16. Abstract (Limit: 200 words)**

A procedure is described for the collection of remote marine aerosol samples by high-volume filtration, cascade impaction, dry fallout collection and rain. Samples were analyzed quantitatively for five classes of naturally occurring lipids (n-alkanes, wax esters, fatty alcohols, sterols, and fatty acids) and polycyclic aromatic hydrocarbons (PAHs). Air samples (4,000-10,000 $m^3$) were collected on glass fiber filters under automatic control. Rain samples of 1-5 L were collected on an event basis. Filters and rain samples were extracted with methylene chloride. The extracts were fractionated into discrete chemical classes by silica-gel absorption chromatography. The fractions were derivatized if necessary and analyzed by HRGC and HRGC/MS. A second filter extraction was required for fatty acid salt analysis. Internal standards were used to quantify recoveries and concentrations. Mean recoveries relative to the internal standards were 96.5% for $C_{12}$-$C_{36}$ n-alkanes, 96.4% for $C_{12}$-$C_{30}$ n-fatty acids, 92.5% for $C_{12}$-$C_{30}$ n-fatty alcohols and 93.3% for cholesterol. Typical blanks and concentrations for remote marine aerosol and rain samples are described and compared with other methods used in coastal marine, rural and suburban sampling locations.

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