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Description of the Analysis of a Wide Range of Volatile Organic Compounds in Whole Air Samples Collected during PEM-Tropics A and B

Jonah J. Colman,^{†,‡} Aaron L. Swanson,[†] Simone Meinardi,[†] Barkley C. Sive,^{†,§} Donald R. Blake,[†] and F. Sherwood Rowland[†]

Department of Chemistry, University of California, Irvine, CA 92697.

A large number of hydrocarbons, halocarbons, and organic nitrates were quantified in whole air samples acquired for the NASA-sponsored GTE missions PEM-Tropics A and B. The samples were collected in electropolished stainless steel canisters from two aircraft while flying over the Pacific Basin. Two nominally identical multicolumn multidetector gas chromatographic analytical systems were employed. Whole air samples were also used as working and calibrated standards and were collected specifically for this purpose. This paper describes the analytical procedure employed during PEM-Tropics B. Minor differences in the PEM-Tropics A system will also be discussed. More than 3900 samples were analyzed for 34 gases during PEM-Tropics A, over 4500 samples were analyzed for 58 gases during PEM-Tropics B. An overview is presented of the collection, analysis, and quantification of whole air samples during the PEM-Tropics missions, along with an analysis of the analytical precision achieved during these missions.

Hydrocarbons, halocarbons, and organic nitrates were quantified from whole air samples collected as part of the global tropospheric experiment (GTE) Pacific Exploratory Mission (PEM) Tropics A and B. Each mission consisted of around 40 flights on two aircraft, a DC-8 and a P-3B. PEM-Tropics A took place between August 5 and October 6, 1996; PEM-Tropics B, between March 6 and April 18, 1999. The PEM-Tropics missions were designed to study atmospheric chemistry within the Pacific Basin. Areas of operation for the aircraft included Christchurch (New Zealand), Christmas Island, Easter Island, Fiji, Guayaquil (Ecuador), Costa Rica, Honolulu, and Tahiti.¹ Over 3900 whole air samples were collected during PEM-Tropics A, and over 4500 during PEM-Tropics B; all of these were subsequently analyzed by gas chromatography at UC Irvine. In total, ~400 000 individual pieces of data were archived. Table 1 lists the compounds quantified for PEM-Tropics B. The wide ranges of source distributions and residence times spanned by the compounds that were

quantified lend themselves to the analysis of many important questions in atmospheric chemistry, such as stratospheric ozone loss, tropospheric ozone production, the impact of natural vs anthropogenic sources, and global oxidative capacity.

The Blake/Rowland research group has performed trace gas analysis of whole air samples at UCI since 1977. While sampling whole air, a wide range of environments and airmass histories may be encountered and, thus, a correspondingly large range of compound abundances and ratios. An unusual environment (or airmass history) may present an unexpected (or unknown) coelutor, which could affect quantification. The procedures employed to alleviate these difficulties have changed over time as new ideas or new technology have been introduced. Examples include metering an aliquot of an airmass as a pressure change, and employing a mass-selective detector. The primary absolute standards that are utilized have not changed. Thus, all of the data produced by the Blake/Rowland group are on the same absolute scale. The canisters employed for whole air sampling were manufactured by the group and are currently a seventh generation design. Canisters are conditioned and tested regularly to ensure reliability. Each gas reported has been tested for stability in our canisters with the exception of dimethyl sulfide (DMS), which was quantified for the first time during PEM-Tropics B and was added to the analysis list post hoc. At present, thousands of samples are collected and analyzed, for a variety of projects, every year. The projects entail both ambient and pressurized sampling, either ground-based or from aircraft, in both remote and urban regions. The system described here is used for all analyses.

The air samples analyzed for the PEM-Tropics missions were collected from aircraft moving at an average velocity of 200 m/s. The fill time, which varied with the ambient pressure outside the plane, ranged from 20 s to 2 min and averaged 1 min. Thus, each sample canister was filled over a spatial distance averaging 12 km. Within this spatial range, air may be sampled from parcels with different temporal/spatial histories, especially when the aircraft is moving in the vertical plane. Thus, each sample is already an average of the air encountered along that 12 km trajectory. The total geographic range covered by the missions was approximately 130° longitude, 120° latitude, and 12 km altitude. The Pacific Basin represents one of the most remote sites (from human influences) remaining on the earth, and so it is likely to be a good place to study the impact of humanity on global atmospheric chemistry, both from the perspective of what condi-

[†] University of California, Irvine.

[‡] Current address: Los Alamos National Laboratory, MC 305, Los Alamos, NM 87545.

[§] Current address: Department of Chemistry, Central Michigan University, Mt. Pleasant, MI 48859.

(1) Details about the PEM missions can be found at http://www.gte.larc.nasa.gov/pem/pemt_hmpg.htm and links therein.

Table 1. Range of Sample Values and Standard Mixture Values^a

name	formula	LOD	min	max	PONT B ^b	2 NIK ^c	BR ^d	CYC ^e
HFC-134a	CH ₂ FCF ₃	1	6.4	22.2	7.0		27.6	11.4
HCFC-22	CHClF ₂	1	122	171	135	118	174	138
HCFC-142b	CH ₃ CClF ₂	1	9.4	15.8	11.7	3.9	17.4	13.3
HCFC-141b	CH ₃ CCl ₂ F	1	8.1	19.0	9.1	1.1	22.0	11.5
CFC-12	CCl ₂ F ₂	10	523	559	534	517	546	499
CFC-11	CCl ₃ F	1	252	340	265	270	258	242
CFC-113	CCl ₂ FCClF ₂	1	78	85	82	113	81	112
CFC-114	CClF ₂ CClF ₂	1	13.2	14.8	14.1	13.8	15.2	14.6
methyl chloride	CH ₃ Cl	5	497	828	530	485	533	539
methyl bromide	CH ₃ Br	1	6.9	11.9	11.0	10.0	35.4	15.2
methylene chloride	CH ₂ Cl ₂	0.1	5.3	117.1	22.1	61.1	58.2	33.5
chloroform	CHCl ₃	0.1	3.9	47.4	8.7	14.0	12.8	11.6
methyl chloroform	CH ₃ CCl ₃	1	56.9	67.4	82.5	197	72.2	88.3
carbon tetrachloride	CCl ₄	0.1	98	103	103	67.0	95	93
1,2-dichloroethane	CClH ₂ CClH ₂	0.05	LOD ^f	25.7	2.23	3.97	2.46	3.34
perchloroethene	C ₂ Cl ₄	0.05	0.33	26.4	4.77	36.5	49.8	24.6
H-1211	CBrClF ₂	0.05	3.50	9.7	3.70	2.61	4.39	3.62
H-2402	CBrF ₂ CBBrF ₂	0.05	0.43	0.53	0.49	0.46	0.49	0.50
DMS	CH ₃ SCH ₃	1	LOD	372	1.6			
methyl iodide	CH ₃ I	0.01	LOD	1.38	0.21	0.26	2.09	1.73
methylene bromide	CH ₂ Br ₂	0.01	0.41	2.55	0.78	0.76	1.06	1.49
bromoform	CHBr ₃	0.01	0.02	5.35	0.57	0.27	2.17	5.75
bromochloromethane	CH ₂ BrCl	0.01	0.08	1.35	0.24	2.10	0.51	0.83
dibromochloromethane	CHBr ₂ Cl	0.01	LOD	0.38	0.16	0.15	0.47	0.98
bromodichloromethane	CHBrCl ₂	0.01	0.02	0.33	0.16	0.53	0.70	0.44
methyl nitrate	CH ₃ ONO ₂	0.01	0.86	53.3	4.29	1.46	9.31	12.1
ethyl nitrate	C ₂ H ₅ ONO ₂	0.02	0.10	17.6	6.84	2.50	12.4	11.8
<i>i</i> -propyl nitrate	<i>i</i> -C ₃ H ₇ ONO ₂	0.02	LOD	66.3	4.58	0.51	21.2	9.90
<i>n</i> -propyl nitrate	<i>n</i> -C ₃ H ₇ ONO ₂	0.02	LOD	9.08	1.61	0.22	4.71	3.96
2-butyl nitrate	2-C ₄ H ₉ ONO ₂	0.02	LOD	100.2	2.06	0.71	18.9	8.20
ethane	C ₂ H ₆	3	137.0	12927	776	3828	2263	1614
ethene	C ₂ H ₄	3	LOD	5849	67	289	523	188
ethyne	C ₂ H ₂	3	5.7	5360	109	364	1048	552
propene	C ₃ H ₆	3	LOD	1740	44.0	95	16.7	29.0
propane	C ₃ H ₈	3	LOD	7330	1088	2413	2023	526
cyclopropane	C ₃ H ₆	3	LOD	18.3	7.6	27.5	15.2	12.7
<i>i</i> -butane	<i>i</i> -C ₄ H ₁₀	3	LOD	1847	9.9	417	289	110
propadiene	C ₃ H ₄	3	LOD	121	LOD	LOD	17.5	5.5
<i>n</i> -butane	<i>n</i> -C ₄ H ₁₀	3	LOD	2400	15.7	957	507	286
<i>i</i> -2-butene	<i>i</i> -2-C ₄ H ₈	3	LOD	139	15.1	6.9	0.55 ^g	0.65 ^g
1-butene	1-C ₄ H ₈	3	LOD	259	2.21 ^g	25.0	3.69	5.12
<i>i</i> -butene	<i>i</i> -C ₄ H ₈	3	LOD	274	21.9	LOD	17.2	118
<i>c</i> -2-butene	<i>c</i> -2-C ₄ H ₈	3	LOD	130	LOD	LOD	4.6	3.2
<i>i</i> -pentane	<i>i</i> -C ₅ H ₁₂	3	LOD	2113	15.3	459	509	167
<i>n</i> -pentane	<i>n</i> -C ₅ H ₁₂	3	LOD	789	8.8	357	248	96
3-methyl-1,3-butadiene	C ₅ H ₈	3	LOD	274	LOD	180	3.6	2.0 ^g
<i>n</i> -hexane	C ₆ H ₁₄	3	LOD	488	7.60	107	65.2	27.6
cyclohexane	C ₆ H ₁₂	3	LOD	194	1.53 ^g	19.5	38.9	13.4
benzene	C ₆ H ₆	3	LOD	1057	25.9	109	226	140
<i>n</i> -heptane	C ₇ H ₁₆	3	LOD	225	1.63 ^g	28.7	16.0	8.83
toluene	C ₇ H ₈	3	LOD	4607	18.5	131	285	168
<i>n</i> -octane	C ₈ H ₁₈	3	LOD	143	LOD	15.9	16.9	6.43
ethylbenzene	C ₈ H ₁₀	3	LOD	622	2.34 ^g	11.4	49.7	24.7
<i>m</i> -xylene	C ₈ H ₁₀	3	LOD	1298	5.8	10.7	111	64
<i>p</i> -xylene	C ₈ H ₁₀	3	LOD	535	2.5 ^g	6.4	52	29.6
<i>o</i> -xylene	C ₈ H ₁₀	3	LOD	750	4.12	9.31	77.8	42.8
2,2,4-trimethylpentane	C ₈ H ₁₈	3	LOD	18.3	2.39 ^g	LOD	68.2	20.1
2,3,4-trimethylpentane	C ₈ H ₁₈	3	LOD	LOD	LOD	3.3	17.3	3.09

^a All values are presented in units of parts per trillion by volume. ^b PONT B refers to the calibrated standard collected in White Mountain, CA. Used for halocarbon quantification. ^c 2 NIK refers to the calibrated standard collected near La Jolla, CA. Used for hydrocarbon quantification. ^d BR refers to the working standard collected near Escondido, CA. ^e CYC refers to the working standard collected near Cayucos, CA. ^f "LOD" indicates data that is below our stated limit of detection. ^g Note that these values are below our stated detection limit. They were determined using alternate procedures (e.g., larger sample aliquot).

tions were like before industrialization, and how humanity is changing them. It is also a unique place to study the impact of the ocean on atmospheric chemistry; however, its distance from anthropogenic and terrestrial source locations also leads to many gases with short tropospheric residence times being below detection limit in the majority of samples.

B Analytical Chemistry

EXPERIMENTAL SECTION

The data considered here were produced from samples of air collected on aircraft during PEM-Tropics A and B. The sampling procedures were identical on the two aircraft, the P-3B out of NASA/Wallops and the DC-8 flying out of NASA/Ames (and NASA/Dryden). Air sampling canisters are shipped and analyzed

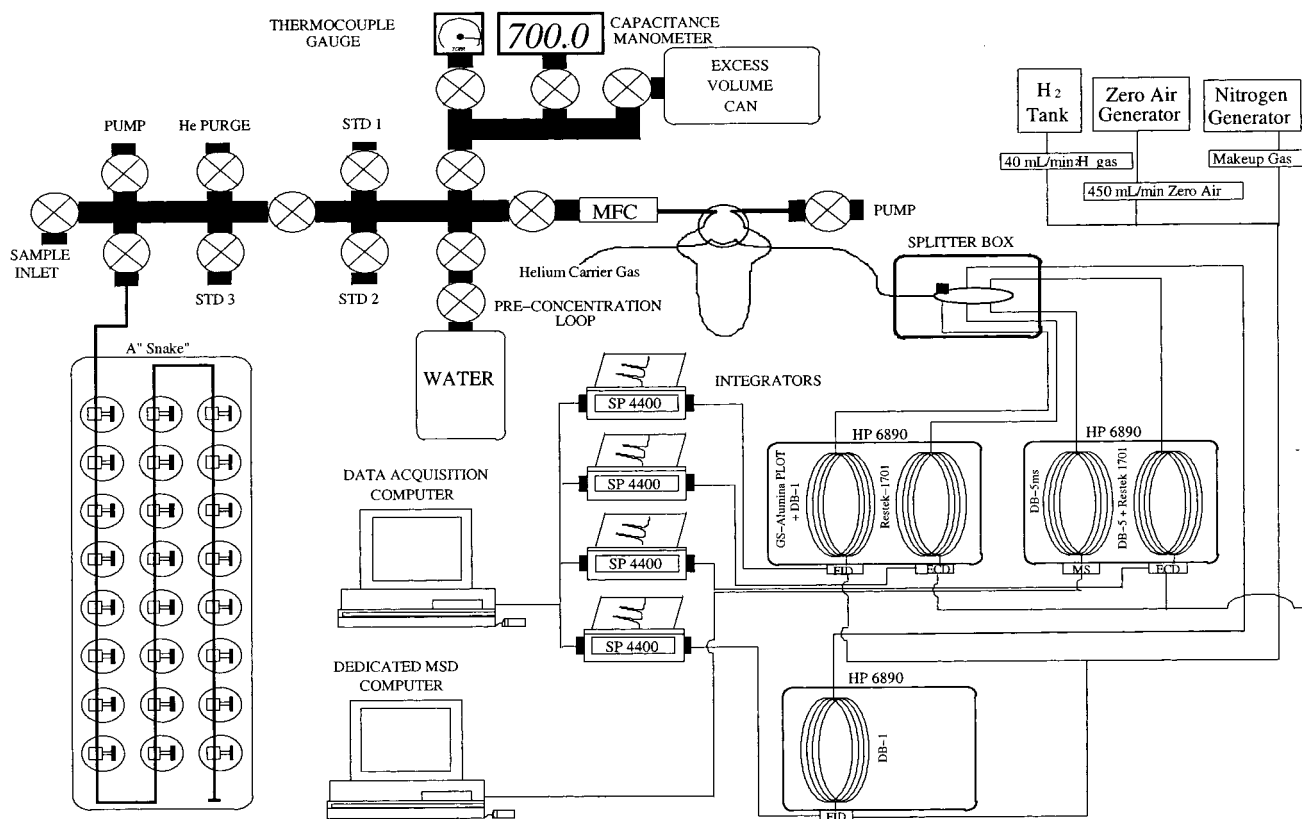


Figure 1. Graphic representation of the chromatographic system configuration used during PEM-Tropics B. Note that there is a snake of 24 sample canisters attached to the system manifold.

together in "snakes" during aircraft missions. Each snake is an assembly of 24 canisters linked in series. The canisters were first linked together in rows of eight using Ultra-Torr union tees and stainless steel tubing, and the three rows of eight were linked using stainless steel flex tubing. Air was drawn from a sample port in the fuselage, through an all stainless steel (grease-free) Parker MB-602 XP bellows pump (with viton gaskets) and sample manifold, and into individual evacuated 2-L stainless steel canisters, each equipped with stainless steel bellows valves and containing 17 Torr of water (roughly the vapor pressure of water at room temperature). The canisters were pressurized to 40 psig and returned to UC Irvine for subsequent chromatographic analysis, typically within 2 weeks of collection. The chromatographic systems remained in operation 24 h a day during the course of the project analysis. Continuous operation helps to stabilize the analytical systems and, thus, to produce an internally consistent data set.

Two separate but equal analytical systems were employed for each mission, PEM-Tropics A and B. In this paper, the systems used during PEM-Tropics B will be described first, then differences in the PEM-Tropics A systems will be delineated. Figure 1 shows a graphic representation of the system configuration used during PEM-Tropics B. For analysis, snakes were connected to the system, and the interim volumes were evacuated. Approximately 800 Torr of air from an individual canister was introduced into the system manifold. Subsequently, 700.0 Torr of this sample was passed over glass beads (1/8-in. diameter, washed with acetone and heated at 350 °C overnight) maintained at liquid nitrogen temperature; the rest was discarded. This procedure corresponds to a 1519 cm³ sample aliquot at standard temperature

and pressure. A Brooks Instrument mass flow controller model 5850E was used to regulate the flow, which was kept below 500 cm³/min to ensure complete trapping of the relevant components and to prevent freeze-up. This procedure has the effect of preconcentrating the relatively less volatile components of the sample (such as halocarbons and hydrocarbons) while allowing volatile components (such as N₂, O₂, and Ar) to be pumped away. The less volatile compounds were then revolatilized by immersing the sample loop in hot water (~80 °C), and subsequently flushed into a helium carrier flow (head pressure, 48 psi). This sample flow was then reproducibly split into five streams at a 1-to-6-port union (Valco Instruments, 1/16-in. manifold 1 to 6 ports, 0.75-mm inlet bore, 0.25-mm outlet bore, with one outlet port capped off). Each stream was chromatographically separated on an individual column and sensed by a single detector. Three HP 6890s form the core of each analytical system that was used during PEM-Tropics B. Electron-capture detectors (ECD, sensitive to halocarbons and alkyl nitrates), flame-ionization detectors (FID, sensitive to hydrocarbons), and quadrupole mass spectrometers (MSD, for unambiguous compound identification and selected ion monitoring) were employed.

The first HP-6890 (GC-1) in a system contains two columns. The first column is a J&W DB-5 (30 m; i.d., 0.25 mm; film, 1 μm) connected in series to a RESTEK 1701 (5 m; i.d., 0.25 mm; film, 0.5 μm), which was output to an ECD detector. The DB-5/RESTEK 1701 union helps to resolve halocarbon and organic nitrate species that have similar polarity through higher retention of the nitrate species. The second column is a DB-5ms (60 m; i.d., 0.25 mm; film, 0.5 μm), which was output to an MSD detector (HP-5973). The DB-5/RESTEK 1701 received 6.84% of the total

Table 2. Oven Parameters^a

	GC-1	GC-2	GC-3
init temp, °C	−30	−50	−20
init time, min	1.50	1.50	1.50
rate 1, °C/min	15	18	20
final temp 1, °C	50	30	200
final time 1, min	0	0	4.70
rate 2, °C/min	10	13	
final temp 2, °C	110	145	
final time 2, min	0	0	
rate 3, °C/min	20	25	
final temp 3, °C	200	200	
final time, min	0.00	0	
tun time, min	17.33	16.99	17.20

^a The designations GC-1, GC-2, and GC-3 are described in the text.

carrier flow, and the DB-5ms received 10.1%. The second HP-6890 (GC-2) contains a J&W DB-1 column (60 m; i.d., 0.32 mm; film, 1 μ m) output to an FID detector. This column received 15.1% of the flow. The third HP-6890 (GC-3) contains a J&W GS-Alumina PLOT column (30 m; i.d., 0.53 mm) connected in series to a DB-1 (5 m; i.d., 0.53 mm; film, 1 μ m), which was output to a FID detector, and a RESTEK 1701 (60 m; i.d., 0.25 mm; film, 0.50 μ m), which was output to an ECD detector. The PLOT/DB-1 union helps to reduce signal spikes from PLOT column bleed and tightens up the CO₂ peak width. The GS-Alumina PLOT column received 60.8% of the flow, and the RESTEK 1701 received the remaining 7.16%. The oven parameters employed for each GC are listed in Table 2; liquid nitrogen was used to achieve subambient initial temperatures.

The signal from each FID and ECD detector was output to a Spectra Physics 4400 integrator, which produced hardcopies of the analogue response, and to a personal computer, where it was recorded digitally using Labnet software (Spectra Physics, San Jose, CA). Each MSD detector was output to a dedicated personal computer and digitally recorded using Chemstation software (Hewlett-Packard, Palo Alto, CA). Each resulting chromatogram was manually modified, and each peak shape individually checked. This type of quality control is labor intensive, but it is considered indispensable for datasets of this size. While sampling whole air, one may encounter a large range of compound abundances and potential coeluturs that could affect quantification. In addition, while running several thousand samples continuously, column characteristics can degrade, thus changing retention time or peak shape. This can be due to either column aging or problems involving retention of an unusual compound injected during the previous run. A slight change in retention time or peak shape can cause large errors for a completely automated quantification, but they are readily identified by trained analysts.

Zero-air and nitrogen for use in the FID and ECD detectors were generated in the lab. House air was passed through a homemade glass wool filter, and then through a Whatman 64-02 air-dryer equipped with a 100-12 BX prefilter. This removes oil, water, and any particulates from the air stream, which is then split and directed into a Domnick Hunter nitrox-nitrogen generator (NG7-0) and a Praxair zero-air generator (model Airlab WHA 76803). The output from these devices was then split further and

directed into gas regulators for head pressure regulation. Before entering the analytical system, all gases that were employed were passed through a homemade graphite/molecular sieve trap to remove any remaining contaminants; in the case of helium and hydrogen (ultrapure, purchased by the cylinder) an identical trap that was kept immersed in liquid nitrogen was connected in series. These traps were preconditioned (and regenerated) by flowing hydrogen gas through them at a temperature of 350 °C for at least 24 h. Both of our FIDs operate at a detector temperature of 250 °C with a zero-air flow of 450 mL/min, an H_{2(g)} flow of 40 mL/min, and a detector makeup gas flow of 20 mL/min N_{2(g)}. The ECDs operate at a detector temperature of 250 °C with a detector makeup flow of 50 mL/min N_{2(g)}.

During the PEM-Tropics A mission, the physical set up and operation of the systems was almost identical. However, the HP 6890s, the HP 5973 mass spectrometer, the nitrogen generator, and the zero-air generator were added for PEM-Tropics B. During PEM-Tropics A, ultrapure gases were purchased by the cylinder; their output was handled in the same way as that of the gas generators during PEM-Tropics B. Each system was based on 3 HP 5890 II GCs, and in place of the MS detector, there was a third ECD detector. The HP 5890s did not have built-in mass flow controllers for regulating detector feed gases, and so additional flow controllers were used for this purpose. In addition, the 5890-based HP ECDs were roughly an order of magnitude less sensitive than the new 6890 ECDs. Thus, during PEM-Tropics A, an ECD makeup gas that was 99.95% N_{2(g)} and 0.05% O_{2(g)} was employed. This technique, known as oxygen doping, enhanced the sensitivity of the ECDs toward hydrogen containing halocarbons and organic nitrates. The cost associated with this technique was accelerated degradation of the detectors as well as the need for eight additional mass-flow controllers to control mixing ratios of N_{2(g)} to O_{2(g)}. The carrier gas employed during PEM-Tropics A was hydrogen; helium was employed during PEM-Tropics B. This was found to help to improve the baseline of the MSD detector and, thus, decrease the associated detection limit and increase precision for many compounds.

The relative flow passing through an individual column in the system depends primarily on its inner diameter. Because one carrier gas line feeds all columns through the 6-port splitter manifold, each column's flow rate is tied to the relative restriction of flow into the other columns at the splitter. The carrier gas head pressure was set at 48 psig. This pressure was set to achieve the approximate void volume elution times desired for each column at the starting temperature. The intent was to split the flow among the channels in such a way as to facilitate detection of a variety of halo- and hydrocarbon species at typical ambient mixing ratios. The majority of the flow was directed to the PLOT column due in part to the lower per-molecule sensitivity of the FID detector (vs ECD or MSD), and the low ambient levels of many nonmethane hydrocarbons in the remote South Pacific. The split ratios were found to be highly reproducible as long as the specific humidity of the injected air was above 2 g H₂O/kg air (roughly 10 Torr for a canister pressurized to 40 psig). For this reason, as well as to increase the stability of certain compounds in our canisters,² 17 Torr of water was added to each (preconditioned, evacuated)

(2) Yokohata, A.; Makide, Y.; Tominaga, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1308-1314.

Table 3. PEM-Tropics Accuracy^a

name	ave PEM-Tropics A, 1996	ave PEM-Tropics B, 1999	WMO values, 1996 ^b	WMO 1996 growth rates ^c
HCFC-134a	— ^d	9.0	3.0	1.4
HCFC-22	119	134	122–125	5.0–5.7
HCFC-142b	—	11	7.6	1.1
HCFC-141B	—	9.8	5.4	1.9
CFC-12	524	533	530	4–5
CFC-11	264	260	264–271	–0.7
CFC-113	83	81	83–84	0–0.1
CFC-114	14.0	14.0	—	—
methyl chloride	563	552	550	—
methyl bromide	8.9	8.6	9–11	—
methyl chloroform	84	61	89–97	–13 to –14
carbon tetrachloride	106	100	100–103	–1
H-1211	3.4	3.9	3.4–3.8	0.2
H-2402	0.5	0.5	0.4–0.5	0.01
methylene bromide	0.8	1.0	0.6–1.0	—

^a All values are presented as parts per trillion by volume. ^b Values taken from WMO 98'. ^c Growth rates are in units of parts per trillion by volume per year. ^d — Indicates no data.

canister from a previously degassed reservoir of deionized, distilled water before being sent into the field. It is worth noting that a manifold independent of the sampling manifold, and equipped with multiple pumps, was used for evacuating the preconditioned canisters and adding water to them.

The reproducibility of the split ratio was monitored by examining the mixing ratios calculated for a compound that gives a large signal, has good chromatographic characteristics, and is quantified on multiple detectors. The compound CCl₃F (CFC-11) was quantified at both ECD detectors and the MS detector with high precision, and their relative ratios were examined for every sample and standard. This compound also has the advantageous property that its mixing ratio in the troposphere is quite homogeneous in both time and space. When outliers were observed, the split ratio was deemed at fault and could be adjusted to give relative CFC-11 values equal to the relative mean CFC-11 value. Propane was detected on both FID detectors and was used to monitor the split for the associated columns. This technique was used primarily as a check of the split-ratio stability. Note that because all of the columns are fed from the same carrier gas line, the sum of their individual flows should be conserved even when the split ratios deviate. During PEM-Tropics B, no adjustments were necessary; during PEM-Tropics A, outliers were occasionally observed (<1% of samples). In these cases, the values were either adjusted or not archived.

Calibration. Multiple standards were employed on each system. Working standards were run roughly every 2 h, and calibrated standards were run at least twice daily. Pressurized cylinders of air are regularly collected from different environments and calibrated in-lab for use as standards. Collection involves immersing an evacuated "S-100" scuba tank (conditioned by multiple pump/flush cycles) in liquid nitrogen and pushing air into it with a Parker (MP-602 XP) all stainless steel double-bellows pump for about an hour. This procedure gives ~2100 psi in the tank once it has warmed to 0 °C. The tanks are pressure rated to 3300 psi. The tank is then attached to two (or occasionally more) electropolished aluminum gas cylinders (Scott Marin) and opened to them in series. This procedure is then repeated until all of the gas cylinders are filled to ~2000 psi. The primary reference

standard for halocarbons was previously calibrated from static dilutions of standards prepared in this lab. Its absolute accuracy for a given compound is tied to a manometer measurement and how accurately the appropriate volume ratios for the dilution line used are known.³ For hydrocarbons, a propane standard purchased from the National Bureau of Standards (SRM 1660A) was used to calculate a per-carbon response factor (PCRF) for the FIDs. This was compared to PCRFs calculated from more readily available (and economical) commercial standards (NIST and Scott Marin) to check the absolute accuracy of the commercial standards as well as the appropriateness of using the same PCRF for different compounds. Then from analysis of the commercial standards, a different PCRF was assigned for each alkane from ethane to octane. This PCRF was then used for any compound with an equivalent number of carbons. For example, the PCRF determined for butane was employed during quantification of the butenes. Interestingly, using the PCRF for ethane yielded good results for dimethyl sulfide (DMS) as well, and this result will be reported in a separate publication.⁴

Our calibration scheme has been cross-checked against absolute standards from other groups for both hydrocarbons and halocarbons. Additionally, the group at UCI has participated in the Non-Methane Hydrocarbon Intercomparison Experiment (NOMHICE). In this experiment, it was demonstrated that our analytical procedures consistently yield accurate identification of a wide range of unknown hydrocarbons and produce excellent quantitative results.^{5,6} It is difficult to compare our measurements of hydrocarbons during the PEM-Tropics missions to other groups on an absolute scale because of the gases' short residence times and the remote nature of the sampling locations. Gases with longer residence times are more easily compared with other groups' measurements. Table 3 lists the mean values of our PEM-Tropics A and B data sets, along with global tropospheric averages summarized by WMO 98' in their Tables 1 and 2.⁷

- (3) Wang, C. J.-L. Ph.D. Dissertation, University of California, Irvine, 1993.
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During PEM-Tropics B, groups led by E. L. Atlas at the National Center for Atmospheric Research (NCAR), and H. B. Singh at NASA Ames Research Center, independently measured 15 and 3 of the gases discussed here, respectively. They did not quantify as many samples as the UCI group, but comparison of data collected at roughly the same time and location revealed good agreement. Mean values were within quoted error for all of the compound comparisons except C_2Cl_4 . Concurrent measurements of C_2Cl_4 showed average values of 1.78 pptv vs 2.31 pptv (0.77 Atlas/UCI) for Atlas vs UCI, and 2.02 pptv vs 1.72 pptv (1.17 Singh/UCI) for Singh vs UCI (the UCI scale was in the middle of the Atlas and Singh scales). In this case, nonlinearities in detector response and decreasing precision as our detection limits are approached may have been involved in the differences observed. The absolute accuracy of our measurements for all of compounds that were measured during PEM-Tropics B is estimated as 1–10% at 1σ , increasing along with the precision as our detection limits are approached.

Previous to the PEM-Tropics missions, working standards were collected on the coast north of Cayucos, CA, and inland near Escondido, CA. Calibrated standards were collected at Scripps Pier in San Diego, CA, and at the White Mountain research station, CA. Quantification of the organic nitrates for the PEM-Tropics missions was done in collaboration with E. L. Atlas's group at NCAR. Both groups ran a standard collected near Boulder, CO, for this purpose. Every effort was made to use standards that are representative of air we expect to sample during the mission. However it is difficult to find air as clean as that sampled during the PEM-Tropics missions. Table 1 shows the mixing ratios of the various components of our calibrated standards, along with values for our working standards as determined post hoc during the PEM-Tropics B mission by comparison with our previously calibrated standards. Also shown are the detection limits estimated for our apparatus during PEM-Tropics B and the range of mixing ratios encountered during the PEM-Tropics B mission.

Systematic Temporal Drift. The calibrated standards were employed to put all of the measurements on the same absolute scale and as a check of the working standard. The working standard was employed because of the difficulty involved in calibrating and maintaining a set of "absolute" standards. Thus, their use is minimized whenever possible. The working standard was used to correct the data for drift (on a time scale of tens of hours) in the detector response. This is illustrated in Figure 2A,B. Figure 2A shows working standards that were run between the evening of Julian day 257 and the morning of Julian day 271, 1996. The responses from two different detectors to CCl_2F_2 (CFC-12) are shown plotted versus time. It is clear that one detector was drifting significantly, and the other marginally. Thus, the response factor for use in converting detector response (area units) to mixing ratios was changing with time (because the CFC-12 mixing ratio was constant in the standard). This was confirmed by comparing the amount of drift in the various calibrated and working standards. The drift should have been (and was) the same relative magnitude and pattern in each. This drift must then be

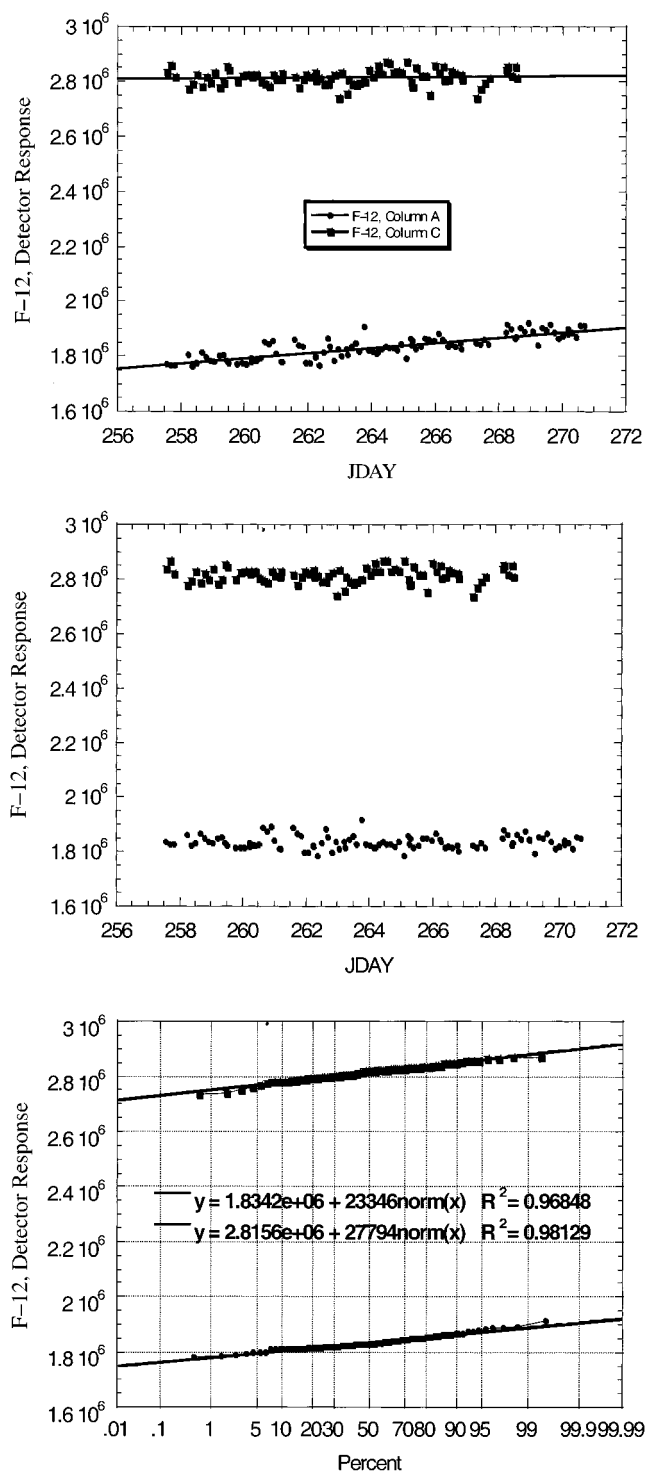


Figure 2. (a) Plot of the working standards run between the evening of Julian day 257 and the morning of Julian day 271, 1996. The responses, from two different detectors, to CFC-12 are shown plotted versus time. Columns A and C are designated as in Table 5. (b) Same data as in Figure 2a after removing systematic temporal drift. (c) Frequency distribution plot for the detrended CFC-12 working standard values shown in Figure 2B.

reflected in our calculations. Figure 2B shows the same data after removing systematic temporal drift.

If the detector drift is not linear over time, then a series of linear fits can be used as an approximation, although in principle, a smooth or weighted fit would be handled in the same way. A

(7) *Scientific Assessment of Ozone Depletion: 1998*; World Meteorological Organization, Global Ozone Research and Monitoring Project – Report No. 44; WMO: Geneva, Switzerland, 1999. Note that data collected by our group, along with data collected by other groups, was used by the WMO working group to arrive at these values.

best-fit line (linear if appropriate) was fit to a plot of the detector response to the working standards vs the time of injection. The fit was then normalized to its mean value to give the relative detector response line. Both working standards were employed for each compound quantified, and their respective relative detector response factor lines were averaged. The relative detector response line was then scaled to the average detector response per mixing ratio calculated from the calibrated standard runs. The White Mountain calibrated standard (Pont B) was typically used for halocarbon quantification and the San Diego calibrated standard (2 NIK), for hydrocarbon quantification. The above procedure assumes that detector response was directly proportional to concentration in the range between the working and calibrated standards (an assumption that is checked) and that only random errors affected the calculated difference. Finally, when quantifying samples, the appropriate absolute response factor for each detector was determined from the appropriately scaled detector response line and the time of sample injection. The detector response to a sample was then divided by this value to give an absolute mixing ratio.

Experimental Precision Analysis. Once the working standard values have been detrended for systematic temporal drift (Figure 2B), they can be used to give an estimate of the precision of the experimental apparatus. As an example, Figure 2C shows a frequency distribution plot for the detrended CFC-12 working standard values shown in Figure 2B. They are well-represented by a normal distribution, as they should be for random experimental error. The mean and standard deviation values extracted from this plot (as the midpoint and slope) can be used to estimate the precision of the experimental apparatus. The one σ precisions of the CFC-12 measurements shown are $23346/1834200 = 1.27\%$ and $27794/2815600 = 0.99\%$. If the output from two or more detectors is averaged to give our reported value (as was often the case, see Tables 4 and 5), then some of the random error will cancel. In our example, the sum is $1834200 + 2815600 = 4649800$ and the absolute error in the sum $[(23346)^2 + (27794)^2]^{1/2} = 36298$. So the relative error in the average is $36298/4649800 = 0.78\%$. The relative error in the standards was calculated for each detrended temporal section for each detector for each compound. In the case in which the relative error of a measurement changed over the course of a mission, an additional fitting function was applied, even if the trend in the average did not change, and the mean of the individually calculated relative errors, weighted by the number of points used to calculate them, was used. When more than one detector output was averaged to give a reported value, the resulting error was calculated as described for CFC-12 above. Supplemental data show the precisions calculated in this way for each compound quantified, on each column, during PEM-Tropics B. Employing all of the working standards run on both systems yields the final precision values presented in Tables 4 and 5.

Although this represents a reasonable way to estimate the precision of our apparatus, it only tells us how precisely a component of a specific mixture (actually in this case two mixtures) of compounds can be measured. That is, because each standard always has the same mixing ratio of an individual compound, any error due to a variable coelutor or due to being on the tail of a variable compound will not be captured. On the

Table 4. PEM-Tropics A Precision

name	system ^a	final precision, % ^b	h. a. ave % ^c	h. a. lowest % ^d
HCFC-22	A	3	2.8	1.8
CFC-12	A, C	0.5	0.5	0.4
CFC-11	A, C, D	0.8	0.8	0.5
CFC-113	A, C, D	2	0.8	0.5
CFC-114	A, C	2	0.8	0.5
methyl chloride	A, B	2	2.2	1.4
methyl bromide	A, C	2	3.8	1.8
chloroform	C, D	3	5.3	2.2
methyl chloroform	A, C	2	1.3	0.7
carbon tetrachloride	A, C	2	1.1	0.8
perchloroethene	A, D	2	11	4.4
H-1211	A, C, D	1	0.8	0.4
H-2402	D	3	2.2	0.9
H-1301	A	1	1.3	0.7
methyl iodide	C, D	3	33	8.4
methylene bromide	A, C, D	5	5	1.8
bromoform	A, D	2	29	17
dibromochloromethane	A, D	8	28	22
bromodichloromethane	D	3	34	7.5
methyl nitrate	D	— ^e	23	4.7
ethyl nitrate	D	—	25	6.7
<i>i</i> -propyl nitrate	D	—	33	8.7
<i>n</i> -propyl nitrate	D	—	52	14
2-butyl nitrate	D	—	73	33
ethane	E	0.5	16	2.5
ethene	E	2	10	5
ethyne	E	1	30	11
propene	B, E	5	—	—
propane	B, E	1	38	18
<i>i</i> -butane	E	2	—	—
<i>n</i> -butane	E	1	—	—
<i>i</i> -pentane	E	2	—	—
<i>n</i> -pentane	E	4	—	—
3-methyl-1,3-butadiene	E	—	—	—

^a Shows which column–detector combination was used to quantify that compound: A = DB-1 + ECD; B = DB-1 + FID; C = DB-5MS + ECD; D = RESTEK-1701 + ECD; E = PLOT + FID. ECD = electron capture detector; FID = flame ionization detector. ^b Precision calculated from the standards as described in the text, displayed as a percentage. Because of nonlinearities in the detector response during PEM-Tropics A, we do not report precision values for the organic nitrates. The values are reported to only one significant figure because of uncertainties related in the text. ^c The average relative standard deviation among the 12 homogeneous airmasses, as described in the text, displayed as a percentage. ^d The lowest relative standard deviation among the 12 homogeneous airmasses (h. a.), as described in the text, displayed as a percentage. ^e — Indicates no data.

other hand, if the compound is present in low abundance in our working standard(s), then the precision may be underestimated by this procedure. See, for example, the butenes in Table 5 for which the working standard values were near (or even below) our limits of detection. These problems can be partially alleviated by the use of multiple column quantification for a given compound to give multiple retention times (to help alleviate coelutor artifacts) and by the use of multiple standards with (ideally) differing mixing ratios that span the measurements. Aside from our primary working and calibrated standards, other in-house whole air mixtures were run roughly twice daily to help detect and trace problems caused by these effects. Because the order of elution is somewhat different on different columns, a compound with problematic chromatography on one column may be resolved on another column. This consideration can be important in deciding how many columns and detectors to employ, and whether to quantify a specific compound on a specific column. Over the

Table 5. PEM-Tropics B Precision Estimates

name	system ^a	final precision, % ^b	h. a. ave % ^c	h. a. lowest % ^d
HFC-134a	MS	5.2	4.8	2.0
HCFC-22	MS	2.0	1.7	1.1
HCFC-142b	MS	3.6	2.7	1.4
HCFC-141B	C, MS	4.2	2.1	1.4
CFC-12	C, D, MS	0.72	0.5	0.4
CFC-11	C, D, MS	0.78	0.6	0.3
CFC-113	C, D	1.2	0.7	0.3
CFC-114	C, D, MS	1.9	1.5	1.1
methyl chloride	B, MS	1.5	1.3	1.1
methyl bromide	C, MS	1.7	2.6	1.8
methylene chloride	MS	4.5	3.4	2.4
chloroform	C, D, MS	1.1	1.5	0.9
methyl chloroform	C, MS	1.0	0.8	0.6
carbon tetrachloride	C	0.7	0.5	0.3
1,2-dichloroethane	MS	3.6	5.1	2.2
perchloroethene	C, D, MS	1.2	4.1	1.6
H-1211	C, D	1.1	0.7	0.6
H-2402	D	2.5	1.4	0.7
DMS	— ^f	—	—	—
methyl iodide	C, D	1.1	6.5	4.0
methylene bromide	C, D	1.6	1.9	1.7
bromoform	C, D	1.6	4.2	2.4
bromochloromethane	C	7.4	11	7.2
dibromochloromethane	D	9.3	8.5	6.9
bromodichloromethane	C, D	2.0	2.8	2.0
methyl nitrate	C, D	1.7	4.5	2.5
ethyl nitrate	C, D	1.4	4.3	2.1
<i>i</i> -propyl nitrate	C, D	1.2	4.2	1.4
<i>n</i> -propyl nitrate	C, D	1.6	5.4	2.7
2-butyl nitrate	C, D	1.4	4.6	1.2
ethane	E	0.50	1.7	0.7
ethene	E	0.70	14	12.0
ethyne	E	0.53	2.6	1.4
propene	E	16	—	—
propane	E	0.74	11	1.6
cyclopropane	E	12	9.9	7.5
<i>i</i> -butane	E	1.1	—	—
propadiene	E	8.3 ^e	—	—
<i>n</i> -butane	E	0.61	—	—
<i>t</i> -2-butene	E	34 ^e	—	—
1-butene	E	24 ^e	—	—
<i>i</i> -butene	E	11	—	—
<i>c</i> -2-butene	E	34 ^e	—	—
<i>i</i> -pentane	E	2.6	—	—
<i>n</i> -pentane	E	4.0	—	—
3-methyl-1,3-butadiene	—	—	—	—
<i>n</i> -hexane	E	6.4	—	—
cyclohexane	E	8.0	—	—
benzene	B, E	1.8	—	—
<i>n</i> -heptane	E	4.4	—	—
toluene	E, MS	3.1	—	—
<i>n</i> -octane	E	12 ^e	—	—
ethylbenzene	E	4.1	—	—
<i>m</i> -xylene	E	9.6	—	—
<i>p</i> -xylene	E	9.6	—	—
<i>o</i> -xylene	E	4.8	—	—
2,2,4-trimethylpentane	—	—	—	—
2,3,4-trimethylpentane	—	—	—	—

^a Shows which column–detector combination was used to quantify that compound: B = DB-1 + FID; C = DB-5 + ECD; D = RESTEK-1701 + ECD; E = PLOT + FID; and MS = DB-5ms + mass spectrometer. ECD = electron capture detector; and FID = flame ionization detector. ^b Precision calculated from the standards as described in the text, displayed as a percentage. ^c Average relative standard deviation among the 12 homogeneous airmasses (h. a.), as described in the text, displayed as a percentage. ^d Lowest relative standard deviation among the 12 homogeneous airmasses (h. a.), as described in the text, displayed as a percentage. ^e These values may be overestimated as a result of low mixing ratios in the associated working standards (see discussion in the text and Table 1 for working standard values). ^f — Indicates no data.

course of a mission like PEM-Tropics, the variety of environments encountered, along with our commitment to manual modification of all chromatograms, often reveals the effects of a variable coelutor on one column. The problematic peak can then be dealt with separately or eliminated from consideration while still potentially allowing quantification of the compound.

Under ideal conditions, the approach to calculating experimental precision outlined above is robust and firmly rooted in probability statistics; however, our experience during PEM-Tropics A was not ideal. For reasons that may never be fully known, the values calculated for the working standards typically had more variability than could be readily accounted for. For example, during PEM-Tropics A, CH₃Br was quantified from the output of two detectors. The working standards quantified at the detector connected to the DB-5MS gave a relative precision of 0.7%, but the detector connected to the DB-1 column gave 10%. Initially, only the output of the DB-5MS/ECD column was going to be employed, because it appeared to be more precise; however, upon inspecting the relative trends between the two CH₃Br sample values and their relative variances under a range of conditions, it was concluded that the calculated precision of 10% from the DB-1/ECD column working standards was spurious and should not be applied to the sample determinations. That is to say, the trends observed in the samples were nearly identical with or without inclusion of the DB-1 column output; thus, the values were averaged to help reduce random error. This increase in variance was seen for a number of compound-column-detector combinations during PEM-Tropics A.

The only obvious difference between quantification of standards and sample canisters was the timing of the water addition. During both PEM-Tropics missions, 17 Torr of water was added to the evacuated canisters before they were taken into the field. During PEM-Tropics A, standards were run from a pressurized gas cylinder, and water was added to the sample manifold just prior to addition of the standard. It has been found that relative humidity is an essential factor in chromatographic reproducibility and detector stability (as well as split-ratio stability). It is also known that some compounds adsorb onto certain metal surfaces and that this effect can be minimized through pacification with water. Because of relative humidity's sensitivity to temperature, the entire analysis is timed down to the last detail. For example, the oven startups are synchronized, and the ovens are allowed to equilibrate at their initial temperatures for at least 20 s before subsequent analyses. Water has a large heat of vaporization, and it may be that the addition of water to the sample manifold just prior to analysis was interfering. In any case, the relative trends of the data reported during PEM-Tropics A for CH₃Br were the same to within expected error with or without using the DB-1 output. Therefore, the reported CH₃Br mixing ratios for PEM-Tropics A reflect the average of the output from the two detectors. The overall standard precision during PEM-Tropics A is estimated to be ~2%. This value was arrived at by comparing trends from the output of each column/detector on individual flights, and over the course of the mission.

During PEM-Tropics B, our standards were run from pontoons (34 L stainless steel vessels) that had 17 Torr of water added to them before the introduction of 40 psi of the standard from a gas cylinder. After equilibration, each 40 psi pontoon allowed for 30

separate analyses of the working standard, which equated to 10 continuous days of analysis. This procedural change has reduced the difference between the working standard estimated precision as outlined above and the precision calculated from reruns of an individual sample or comparing samples taken in a "homogeneous airmass", as described below. Thus, during PEM-Tropics B, there were no spurious working standard precision values that needed special treatment, as outlined above for CH₃Br. This example points out the importance of analyzing standards in a way that is as close as possible to the procedure used for samples. Any remaining differences are ascribed to the fact that the system is often very stable for short periods of time, but the baseline does drift on longer time intervals. In addition, the high-frequency drift is not completely resolved (working standards were run every 2 h). Some of the wide variety of environments encountered during the PEM-Tropics missions may pose more or less of an analytical challenge than others. Measurements of exceptionally clean air will often have a more stable baseline than measurements of urban air. As stated before, it is very difficult to find tropospheric air cleaner than that sampled during the PEM-Tropics missions.

Homogeneous Airmass Values. Another approach to estimating experimental precision is to calculate the relative standard deviation of samples thought to have been collected in a homogeneous airmass. The concept of a homogeneous airmass depends on both the residence time of the compound in question and how precisely it can be quantified. Clearly, a compound can only be well-mixed (homogeneous) within a "box" (airmass) if its residence time in the box is long when compared to the internal mixing time of the box. In practice, when flying around in the free troposphere, homogeneous also means at a constant altitude, because source distributions typically change rapidly with altitude (the atmosphere is vertically stratified). Tables 4 and 5 show estimates of precision from the analysis of standards described in the preceding paragraphs, along with data collected during 12 separate homogeneous airmass encounters for each mission. An average of 22 consecutive samples was collected during each encounter, and a range of altitudes (and relative humidities) is represented (0.3–10 km). The lowest relative standard deviation calculated for each compound is presented along with the average relative standard deviation from all 12 encounters. Note that the "homogeneous airmass" error estimates diverge from the standard precision estimate in the limit of short tropospheric residence times. This is expected, because as mentioned above, the concept of homogeneous airmass depends on the residence time of the compound in question. Occasionally, a sample is rerun a number of times to obtain an estimate of precision, and this is more or less equivalent to the homogeneous airmass estimate of precision. To arrive at our working-standard-derived precision, the sample (or the homogeneous airmass samples) would have to be run periodically over the course of the mission. This is impossible, because each sample canister can only be analyzed a couple of times because of its limited volume. Our standard-derived estimate is an estimate of the precision achieved within the range of the working standards over the course of the entire two-month mission, and the homogeneous airmass estimate is an estimate of the precision achieved during a shorter time interval (6 h or so).

The homogeneous airmass values for CH₃Br during PEM-Tropics A shown in Table 4 support our precision analysis for

that compound presented above. They are much lower than the 10% estimated from the standards run on the DB-1/ECD, or the roughly 7.8% that would have been calculated for the overall standard precision (i.e., by combining the error for the two detectors as outlined for CFC-12 above). Indeed, the lowest homogeneous airmass error of 1.8% is in good agreement with the estimate of 2% taken from comparing sample reproducibility between the two detectors. Additionally, the residence time of CH₃Br is short enough that one might expect some contribution from intrinsic variability even in these homogeneous airmasses.⁸ The longer-lived compounds give results that confirm the utility of an analysis of this kind and support our overall analysis; the homogeneous airmass assumptions apply more closely to them. The standard estimates presented here represent the precision over the course of PEM-Tropics, taking into account the variety of airmasses encountered and changing analytical conditions. Precision can be a factor of 4 or so better under more homogeneous conditions, as is also shown by the lowest relative standard deviation values shown for homogeneous airmasses in Tables 4 and 5.

CONCLUSION

Over 8000 whole air samples were quantified by the analytical group at UCI during PEM-Tropics A and B. The vast majority of these were collected in the South Pacific basin in areas remote from anthropogenic influence. The range of compounds that were quantified enabled differentiation of signals from fossil fuel combustion, biomass burning, liquefied petroleum gas leakage, industrial solvents, oceanic emissions, and generalized urban plumes.^{9,10,11} Each sample was analyzed for 34 individual gases during PEM-Tropics A, and 58 individual gases during PEM-Tropics B, resulting in over 400 000 pieces of data being generated. The collection and use of uncalibrated whole air samples as working standards is described. An analysis of precision shows typical values from 1 to 5%, and the absolute accuracy is estimated as 1–10% (both at 1 σ). All of the data discussed here are available from links to the GTE web page at "http://www-gte.larc.nasa.gov/gte_hmpg.htm#table." The data can also be downloaded directly from the ftp site, "<ftp://ftp-gte.larc.nasa.gov/pub/PEMTROPICSB/>".

SUPPORTING INFORMATION AVAILABLE

The precision of each compound on each individual column for both systems 1 and 2, the final precision for each compound on each system individually, and the range of the working standards employed to estimate the precision. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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