Final Report TRACE-P (UCAR proposal #2000-117, NASA NCC-1-420)

Title: Deployment of a Fast-GC/MS System to Measure C_2 to C_5 Carbonyls, Methanol and Ethanol Aboard Aircraft

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Summary

Through funding of this proposal, a fast response gas chromatograph/mass spectrometer (FGCMS) instrument to measure ≤ C_4 carbonyl compounds and methanol was developed for the NASA GTE TRACE-P (Global Tropospheric Experiment, Transport And Chemical Evolution Over The Pacific) mission. The system consists of four major components: sample inlet, preconcentration system, gas chromatograph (GC), and detector. The preconcentration system is a custom-built cryogen-conservative system. The GC is a compact, custom-built unit that can be temperature programmed and rapidly cooled. Detection is accomplished with an Agilent Technologies 5973 mass spectrometer. The FGCMS instrument provides positive identification because the compounds are chromatographically separated and mass selected. During TRACE-P, a sample was analyzed every 5 minutes. The FGCMS limit of detection was between 5 and 75 pptv, depending on the compound. The entire instrument package is contained in a standard NASA instrument rack (106 cm x 61 cm x 135 cm), consumes less than 1200 watts and is fully automated with LabVIEW™ 6i. Methods were developed for producing highly accurate gas phase standards for the target compounds and for testing the system in the presence of potential interferents. This report presents data on these tests and on the general overall performance of the system in the laboratory and aboard the DC-8 aircraft during the mission. Vertical profiles for acetaldehyde, methanol, acetone, propanal, methyl ethyl ketone, and butanal from FGCMS data collected over the entire mission are also presented.

Background

Oxygenated volatile organic compounds (OVOCs) are important constituents of the troposphere because of their role in key oxidation cycles [*Jeaglé et al.*, 2001, *Singh et al.*, 1995, *Müller and Brasseuer*, 1999, *Wohlfrom et al.*, 1999]. Currently, information on atmospheric distributions of these compounds is limited because only recently have ground-based measurements become common and relatively few measurements have been recorded on aircraft platforms. More complete data on the distribution, sources, and sinks of this compound class will ultimately lead to a better understanding of atmospheric chemistry through improved models that explicitly take into account contributions of these species to the photooxidation mechanisms at work in the troposphere.

A number of methods have been used for quantifying ambient OVOC mixing ratios. The intent here is not to give a comprehensive review of measurement techniques but to briefly overview the subject matter that pertains to this paper. An early but still relevant review on the subject of carbonyl measurements may be found in Vairavamurthy et al., [1992]. At that time, there were a number of competing techniques, ranging from liquid scrubbing chemical derivatization followed by liquid chromatography to spectroscopic methods. None of the techniques had distinguished themselves as reliable for ambient carbonyl determination despite nearly a decade of analytical development. The DNPH (2,4-dinitrophenylhydrazine) cartridge technique has been used extensively during the last decade for ambient measurements of formaldehyde and higher carbonyls. This method was adopted by the United States Environmental Protection Agency (USEPA) for measuring formaldehyde, acetaldehyde and acetone throughout the PAMS (Photochemical Assessment Monitoring Stations) network. PAMS was instituted following the 1990 Clean Air Act Amendments (CAAA). The CAAA required States to establish sites to monitor ozone, oxides of nitrogen (NO_x), and volatile organic compounds (VOCs) in order to obtain more comprehensive and representative data on ozone air pollution in affected areas. Drawbacks to the DNPH technique have been documented in the literature [*Vairavamurthy et al.*, 1992, *Sirju and Shepson*, 1995, *Apel et al.*, 1998] and include high blanks, ozone interference, and the requirement for long sampling times (tens of minutes to hours) to achieve high pptv to low ppbv detection limits.

Gas chromatography has also been used, most commonly in ground-based applications, to measure a number of OVOCs including alcohols, aldehydes (> C_1) and ketones [e.g., *Goldan et al.*, 1995, *Riemer et al.*, 1998, *Apel et al., 2002*]. For a recent compilation of GC techniques used to measure VOCs in ambient air, please see *Helmig et al.*, [1999]. The most commonly used detectors for GC OVOC measurements have been the flame ionization detector (FID) and mass spectrometry (MS). Since the FID detector is nonspecific it is imperative that sufficient peak separation is accomplished through optimized chromatography to minimize the potential for co-elutions of target and non-target VOCs. Excellent examples of this technique can be found in *Schade et al., [2000]* and *Goldan et al., [1995]*. GC-MS has become an increasingly popular technique for ground-based studies of OVOCs [*e.g., Helmig et al., 1994, Yokouchi et al., 1994, Montzka et al., 1993, 1995, Liebrock and Slemr, 1997, Biesenthal et al., 1997, Starn et al., 1998, Riemer et al., 1998, and Apel et al., 2002*]. High sensitivity and excellent selectivity are

characteristic of modern GC-MS systems. Other techniques that have been developed and deployed include GC/Atomic Emission Detection (GC/AED) [*Apel et al., 1998 and Greenberg et al., 1999*] and GC/Reduction Gas Detector (GC/RGD) [*O'Hara and Singh, 1988*].

Airborne atmospheric chemistry experimental platforms have become more sophisticated in recent years [*http://www-gte.larc.nasa.gov, http://topse.acd.ucar.edu/*]. These platforms are capable of high spatial coverage over an abbreviated time period. Important information on distributions of key atmospheric species can be gained in a single campaign. Requirements for aircraft-based measurements are more stringent than for ground-based measurements. The highest possible temporal resolution and sensitivities are desired. A number of techniques have been developed to measure OVOCs aboard aircraft. Chemical Ionization Mass Spectrometry (CIMS) techniques have been deployed on a number of missions to measure OVOCs in the troposphere [*Arnold et al., 1986, 1997, Möhler et al., 1993, Wohlfrom et al., 1999, Warneke et al. 2001, Sprung et al., 2001*]. These techniques are characterized by relatively good sensitivities (tens of pptv) and time resolution (seconds to 1 minute). Selectivity is a concern with the single quadrupole CIMS techniques since the ion (or ions) being monitored for quantification may not be unique for the compound (or compounds) of interest. The GC/RGD technique has been used by *Singh et al.* [*1994, 1995, 2000, this study*] to measure acetone and other OVOCs in the upper troposphere. The RGD detector has been shown to be about a factor of ten times more sensitive than the FID for carbonyls [*O'Hara and Singh, 1988*] and is also more selective. Although proven to be a viable technique by *Singh et al.* [*1995*], less than optimal chromatography appears to be a characteristic feature [*C. Stroud, personal communication*] and strict attention to operational details is necessary for quantitative and reproducible results. Recently, an FTIR spectrometer has been deployed to study biomass-burning plumes [*Yokelson et al., 1999*]. An advantage of this system is that many compounds can be observed simultaneously with high temporal resolution. A drawback is that the sensitivity is significantly lower than some of the other techniques.

In implementing any of the techniques described above, experimentalists must be aware of the potential for artifact formation either in the inlet or in the analytical system itself and of difficulties in efficient transfer of these polar compounds through the inlet and into the analytical system. Artifact formation when sampling carbonyl compounds is discussed in *Vairavamurthy et al.*, [*1992*]; ozone, sulfur dioxide, and nitrogen dioxide are listed as potential interfering

compounds. Others have mentioned artifact formation [*Goldan et al., 1995; Riemer et al., 1998*]; however documented tests to isolate and quantify the artifacts are missing in the literature.

There have been few instrument comparisons of carbonyl measurement techniques and none that we are aware of for alcohols. *Apel et al.* [*1998*] have recently reported on a ground-based comparison of GC-MS instruments with cartridge-based techniques for the measurement of carbonyl compounds. Differences greater than a factor of two in the data were common and it was noted that a more formal intercomparison of techniques would be desirable. More recently a CIMS technique and a GC based technique simultaneously measured acetone aboard an aircraft over the North Atlantic free-troposphere and lower stratosphere [*Wohlfrom et al., 1999*]. In this experiment the acetone data obtained by both instruments in the same air masses agree to within approximately 50%.

For TRACE-P, we developed and deployed the first airborne GC/MS system for OVOC measurements. This technique has a number of advantages. It is as sensitive as the RGD detector but is more selective and is capable of measuring a number of different compound classes in addition to OVOCs, including halocarbons and non-methane hydrocarbons (NMHCs). A description is given of the design and operation of this aircraft technique. Data is presented to demonstrate the feasibility of this method.

Experiment

The GC/MS method reported here is similar in basic operating principle to ground-based techniques that investigators have developed. The differences are that a more sophisticated inlet is needed for aircraft sampling; the cryogenic preconcentrator must be extremely efficient to allow rapid sample enrichment and must also be conservative in its consumption of cryogen because of the limited cryogen available on aircraft; the gas chromatograph must be miniaturized; the system must be able to withstand significant vibrations and G-forces; the zero/calibration system must provide periodic calibration and zeros for the inlet while maintaining ambient humidity; the system must be fully automated, and the response time must be rapid. The various components of the system will be described in subsections below.

1. Inlet and sampling system

A schematic of the inlet and sampling system is shown in Figure 1. The inlet consisted of two ports extending approximately 35 cm orthogonal from a window plate of the DC-8 aircraft through an aerodynamic housing. The inlet length was determined by the requirement to sample beyond the boundary layer of the aircraft. The forward port (port 1) served as the inlet to the FGCMS system. It consisted of an electropolished stainless steel (ss) tube extending 0.75 cm beyond the housing into the ambient atmosphere. A temperature-controlled (50 °C) copper block encased the ss tube near the tip of the inlet. Within the housing, the inlet tube was coupled to a heated 0.64 cm O.D. Silonite™ fused silica lined ss tubing that extended to the FGCMS. The aft port (port 2) was the inlet for the zero air/calibration system that will be described later. The inlet tip was a machined piece of aluminum (0.5 cm O.D.) extending 1.25 cm from the housing into the ambient atmosphere. A non-heated 0.64 cm O.D. Teflon™ tube connected port 2 to the zero air generator/calibration (ZA/CS) system.

The inlet was designed so that three functions could be performed: zeroing, calibrations, and ambient air sampling. Zeroing of the inlet was performed by scrubbing ambient air taken in from port 2 with the on-board zero air generator (described below) and returning the scrubbed air towards the front of port 1 and overfilling the inlet, i.e., providing 20% - 50% more flow of scrubbed air than air taken in to the FGCMS from port 1. Calibrations were performed in much the same way with the only difference being that a metered flow of calibration standard was introduced into a known flow rate of the scrubbed air prior to returning the scrubbed air to the inlet. For ambient air sampling, the valve leading to the ZA/CS was shut off and ambient air was taken, by way of a Teflon diaphragm pump (KNF Neuberger Model NO35STI), into the FGCMS analytical system.

2. Cryogenic Preconcentrator

A number of different approaches have been used to preconcentrate VOC compounds for GC analysis. *Helmig at al., [1999]* gives a summary listing of techniques that have been used. Rapid sample cycles and the desire for artifact-free analyses were driving forces behind choosing a fully cryogenic concentrator for this work. An additional requirement for aircraft–based systems is low liquid nitrogen (LN_2) consumption. With these prerequisites and no commercial or

research technology that met our design criteria, a novel preconcentration system was designed and subsequently built.

Key components of the preconcentrator are shown in Figure 2. It consists of a custom-built 10-liter dewar (Cryofab, MA) that has three coils situated near the bottom. Each coil provides cooling to one of three traps, the water trap, the enrichment trap, and the cryofocuser. Nitrogen gas from the LN_2 dewar headspace enters the coils that are immersed in liquid nitrogen. Flowing the cooled nitrogen gas through the heat exchange coils, which are directly connected to the traps, provides rapid cooling for each of the three traps. Temperatures are measured with thermocouples which serve as inputs to a Watlow^{TM} CLS 216 temperature controller described in section 6. The Watlow controlled the trap temperatures by servoing the mass flow controllers through an external digital to analog converter. An important characteristic of this system is that all control devices for phase fluids are at ambient temperature. During sample collection, the water trap temperature was maintained at -15 ± 1 °C and the enrichment trap at -110 ± 1 °C. During sample transfer to the cryofocuser, the water trap was heated to 60 ± 1 °C and the enrichment trap was heated to 100 ± 1 °C. The cryofocuser was maintained at -120 ± 1 °C during sample transfer and was heated to 110 ± 1 °C during injection. The total liquid nitrogen consumption rate was approximately 0.5 liters hr^{-1}. Both standards and ambient air samples were used to characterize the optimal preconcentration parameters prior to deployment.

3. Gas Chromatograph

A custom-built gas chromatograph was used in this study. The dimensions of the unit were 18 cm x 18 cm x 10 cm. The body of the GC oven was constructed of machined Marinite^{TM} M insulator material. Inside the oven a ss mandrel served as a support for the GC column and for a flexible heater element situated on the opposite side of the column. The faceplates were made of stainless steel with channels cut to allow airflow through the oven body. On each face a ss shutter was mounted having matching open channels (with faceplates) to allow airflow through the GC oven during the cooling cycle and to close off airflow during the heating cycle. All temperatures including the oven temperature were controlled through a Watlow CLS-216 capable of controlling up to 16 separate temperature zones (see Section 6). To return to the starting point temperature in preparation for the next GC run, the heater was shut off, a solenoid fired to open the shutter and a fan (1500 L $minute^{-1}$) was turned on.

4. Detector

The FGCMS uses a shock-mounted Agilent Technologies 5973N quadrupole mass spectrometer system. The only modification was to the vacuum system. Agilent equips the system with an Edwards EXT 250 turbomolecular pump that has a pumping capacity of 220 L s^{-1} He maximum displacement. Because of metallic bearings, the pump is only rated for 1 G (gravity force). Therefore, this pump was replaced by a Varian Model V301 NAV (220 L s^{-1} He maximum displacement) turbomolecular pump with all ceramic bearings, rated to 3 G's. This change required the addition of a Varian turbo pump controller and also required the modification of the pump control electronics of the 5973N. The mass spectrometer was operated in the electron ionization single ion mode throughout the study. A laptop personal computer running HP Chemstation™ software controlled the system.

5. Zero air/ Calibration System (ZA/CS)

Establishing good zeros and obtaining accurate calibrations is at the heart of quantitative measurements. We tested a number of commercially produced ultra high purity zero air generation systems, hydrocarbon-free cylinder air, and cylinder N_2 sources and found that for the TRACE-P work, the trace levels of carbonyls in the cylinders were variable and often at unacceptable levels. We have also found that transmission of OVOCs through sampling lines is facilitated greatly by having humidity in the gas stream. A solution to these problems was to build a catalytic zero air generator that scrubs OVOCs to limit-of-detection values while maintaining ambient humidity levels. Figure 3 shows a schematic of the system. Ambient air is drawn through a 2 μm ss filter (Swagelok®, SS-4FW-2) into the ZA/CS through a KNF Neuberger Teflon diaphragm pump (UN828ANDC). After exiting the pump, the air passes through a "T" fitting that houses a poppet valve set to 20.7 kPa. This allows the pump to operate at full, unrestricted, flow while the ZA/CS may be operating at low flow. The air then passes through a 0.50 L stainless ballast volume which dampens pressure fluctuations due to the pump. Airflow is controlled (0-10 slpm) with an electronic mass flow controller (Tylan, FC-280S) prior to entering the heated catalyst tube (375 °C) packed with platinum pellets (1% weight on 3.2 mm Alumina spheres). The scrubbed air is then passed through another filter (2 μm ss filter, Swagelok®, SS-4FW-2), into a cooling coil, and then to the outlet. During deployment, zeroing

of the system was accomplished by scrubbing ambient air, returning the VOC-free air to the sample inlet (Figure 1), and overflowing the inlet so that only the scrubbed air was sampled.

The system was also configured as a dynamic dilution device. OVOC standards were introduced into a mass flow controller (0 -10 sccm or 0-100 sccm), which, in turn, was teed into the scrubbed air flow. The system was capable of diluting standard mixtures by factors of 10 to 10,000 and it was very accurate because only two calibrated flow controllers were used, the mass flow control of the standard and a 0-10 slpm flow controller for the scrubbed air diluent gas. As with the zero air, the diluted standard samples followed a path identical to the ambient air samples through the analytical system.

Standards for this study were gravimetrically prepared in aluminum cylinders using the same principles employed in a well-established method [*Rhoderick and Zielinski, 1988*]. Nitrogen was the balance gas. Table 1 shows the mixing ratios of the standard (NASA A) used during TRACE-P. Standards were analyzed multiple times in the laboratory before and after the experiment. Mixing ratios for the standards were determined by the gravimetric value and were checked against a number of other standards prepared both by our laboratory and other laboratories. All compounds showed good stability (± 5%) except for acetaldehyde which decreased by ~ 9 %.

Independent methods of standards generation and analysis that agree increase the confidence in the overall accuracy of the standards. We constructed a 6-position device for standards generation based upon permeation tubes and employing gravimetry as the method of calibration. Permeation tubes were available for methanol, acetaldehyde, propanal, acetone, methyl ethyl ketone, and toluene. This system consisted of six independent aluminum ovens, each housing one permeation tube. The ovens are temperature controlled to within ± 0.1 °C. The tubes resided in glass housings with high purity nitrogen continuously flowing over them. A dynamic dilution system was constructed to control, mix and dilute the permeation tube effluent to the ppmv to pptv concentration levels. Although the tubes were factory calibrated, we also characterized them using a Mettler balance capable of measuring to ± 10 μg.

The top panel in Figure 4 shows our analysis of the six tubes at once; however, please note that for quantification our normal procedure is to run each permeation tube separately using a highly characterized diluent flow rate. The bottom panel shows our analysis by GC-FID of a high-pressure

cylinder that was prepared containing acetaldehyde, methanol, ethanol, propanal, acetone, butanal and methyl ethyl ketone. Note that all compound peaks are well resolved and easily quantified. Together with the GC-FID analysis, an independent spectroscopic (FTIR) method was used to ascertain the concentrations of compounds gravimetrically prepared in a high-pressure cylinder at 3.0 ppmv. Table 2 shows the results of the comparison of the high-pressure cylinder preparation results with the permeation tubes and the FTIR analysis. Good comparability was observed for the cylinder preparation and the permeation tubes for methanol and acetone. We did not have reliable permeation tube values for acetaldehyde and propanal; although the initial values we obtained were close to the manufacturer's certified rate, their permeation rates increased over time. This occurred despite the fact that we used N_2 sweep gas and maintained the permeation tubes at 30 °C. The manufacturer (VICI, Houston, TX) is aware that there is a problem with the aldehyde permeation tubes and is working with us to help resolve it. Difficulty in using and preparing permeation tubes for acetaldehyde and other aldehdyes has been noted by others [Singh et al., 1995, Riemer et al., 1998]. No permeation tube values are reported for MEK because at the time of the experiment we had only recently put this tube into our system and hence did not have it long enough to obtain an accurate weight loss over time.

The FTIR values agree within the error of the measurement with the gravimetric cylinder values for all compounds measured except for MEK. The reasons for this are unclear and are being investigated further. The well-characterized 3 ppmv cylinder was checked against the NASA A cylinder (Table 1) via GC-FID; all compounds agreed to ± 5%.

To help ensure the accuracy of our in-flight alcohol and carbonyl measurements we also analyzed carbon tetrachloride, a species that is stable and present at a nearly constant mixing ratio in the troposphere (99 ± 3 pptv, [Blake et al., TRACE-P data archive]), as part of each chromatographic run during the TRACE-P experiment. This allowed us to account for small variations in the volume sampled and the absolute mass spectrometer response.

6. Data Acquisition and Automated Control of Instrument

The FGCMS instrument operation was controlled with a PCI bus desktop computer running a graphical user interface (GUI) written in National Instruments (NI) LabVIEW™ 6i coupled to two PCI bus data acquisition/control cards and a Watlow temperature controller. The cards (NI PXI-6025E) provided 16 channels of 12 bit differential input A/D, 4 channels of 12-bit D/A

analog output and 64 digital I/O lines. The temperature controller provided readout and control of 16 temperature channels. The Watlow controller (CLS200 16 channel) was operated from within LabVIEW™ via a third party software package (Anaview, SEG Software) and connected to the system via a serial port.

The main LabVIEW™ code and five subroutines were structured so A/D, D/A, digital I/O and serial communications were queried/controlled once per second. Each A/D channel was measured 10 times at 1 kHz. The values were then averaged to 1-second means and scaled to proper engineering units. Nine gas flows, 15 temperatures, 13 logic states, and 14 serial stream data channels from the NASA DC-8, constituted 51 parameters which were displayed on the GUI and written at five second intervals into an ASCII text file. The code performed the intricate time sequencing necessary for sample acquisition, water removal, pre-concentration, cryofocusing, GC injection and oven temperature programming. The timing for each of these steps was adjustable on the fly.

7. FGCMS Instrument layout

Figure 5 shows a photograph of the FGCMS instrument. A number of the individual components that are visible from this view are labeled: (1) the ZA/CS, (2) the pumping station, (3) the gas standard and He carrier gas station, (4) the HP5973N mass spectrometer, (5) dewar/preconcentration system, (6) the computer used for system automation, and (7) the box containing the control electronics.

A. Operation of the FGCMS Instrument

Please refer to Figure 1 for this discussion. Ambient air was drawn from the inlet (port 1) to the analytical system. During TRACE-P a KNF Neuberger Teflon diaphragm pump (UN-035STI) was used but has since been replaced with a metal bellows pump (Senior Aerospace, MB-602). The air sample continuously flowed through the inlet and through the 1-liter Silonite™-coated ss holding volume maintained at 760 torr with an MKS Model 640A backpressure regulator. An analytical run was started by switching valve 1, thereby closing off the 1-liter holding volume. Sample was then drawn off the holding volume at a rate of 75 sccm for 80 seconds, yielding a total air sample of 100 cm^3. The sample was passed through the first

stage trap, an 8 cm x 0.32 cm PFA teflon tube maintained at –15 °C which was designed to remove water from the sample. It was then passed into the enrichment trap that consisted of a 7.5 cm x 0.32 cm o.d. silicosteel™ tube filled with silanized glass wool and maintained at –110 °C. It was here that the compounds of interest were initially trapped. Valve 2 was switched, the enrichment trap was heated and helium carrier gas swept the compounds of interest to the cryofocusing trap, a 7.5 cm piece of 0.080 cm silicosteel™ tubing maintained at –120 °C. The cryofocusing trap was then rapidly heated, transferring the compounds of interest to the head of a 10 m, 0.18 mm i.d., 1.4 μm phase thickness DB-624 column. The GC oven was held initially at 35 °C for 30 seconds and temperature programmed at a rate of 25 °C /min until the oven reached 110 °C giving a total run time of 3.5 minutes. The carrier gas flowrate was maintained at 4 sccm using a Tylan FC-280 mass flow controller. The oven cooling time was 1.5 minutes.

Calibrations were performed three to six times each flight.

B. Calibration and Instrument Testing

A 2-meter all-glass manifold was assembled to provide known quantities of VOC and potential interferent species for calibration and testing the FGCMS (Figure 6). Because the instrument was not completed until the second test flight, this testing took place at NCAR after the TRACE-P mission; under normal circumstances the testing would occur prior to the mission. Laboratory air was first scrubbed of VOCs, water, and other trace gases and then calibrated amounts of the species of interest were added. An AADCO Model 737-12 provided up to 30-slpm ultra pure air with less than 1-ppm water and ambient levels of CO_2. Calibrated levels of O_3, SO_2, H_2O and NO/NO_2 could be added to the pure air stream through designated ports on the manifold. Detection techniques, described by Gilpin et al. [1997], were used to continuously monitor the levels of these calibrated trace gas levels within the air stream.

Figure 7 shows an example of the calibration curves that we obtained for the compounds measured during the TRACE-P mission. The curves are shown to be linear and also give an indication of detection limits. Detection limits, determined as five times the baseline noise, are given in Table 3. Ethanol measurements were partially compromised because of an artifact species arising from out-gassing of the KNF Teflon diaphragm pump that partially overlapped the ethanol elution time and contained the same ion as the ion (m/e = 31) used to quantify

ethanol. Because of this, ethanol was not included in the TRACE-P data archive. This problem has since been corrected by replacing the KNF pump with a metal bellows pump. For the other compounds quantified, there were no interferences from any other known atmospheric species that we were aware of. The methodology for ozone artifact testing was not straightforward because, as we have empirically discovered, it is difficult to generate ozone without also co-generating carbonyl compounds. Our first approach was to modify the ozone generator (Thermo Environmental Model 565) to minimize the potential for carbonyl artifact generation by simplifying the gas flow path through the system and replacing all standard tubing with inert tubing. Despite these efforts significant artifact formation when generating ozone was found. We were able to ascertain that artifacts were formed in the ozone generator and not downstream by scrubbing the ozone with granulated KCL after exiting the generator and still observing the carbonyl artifacts; the artifacts were not present when the photolysis lamp was turned off. The solution to this problem was obtained by passing the O_2/O_3 effluent from the ozone generator through a custom designed cryotrap trap filled with glass wool and operated at –140 °C. Under this configuration, the carbonyl artifacts were efficiently trapped while still passing ozone. Ozone concentrations were measured using a Thermo Environmental Model 49 instrument.

Figure 8 shows the results of the post-mission ozone testing of our system as it was configured during TRACE-P. Compounds that showed a response were acetaldehyde, propanal, acetone, and butanal. The alcohols and methyl ethyl ketone were not affected by ozone. In processing our data for the TRACE-P archive, the artifact contribution to the signal, as determined by the laboratory tests, was removed. This was possible because the NASA data archive includes one-second data for ozone. Thus, the artifact contribution from ozone, calculated from the line fits in Figure 8, was removed assuming that the interference response from ozone during TRACE-P was the same as the response during the post-experiment laboratory tests. This, of course, introduces additional measurement uncertainty for these compounds which is accounted for by the error in the function describing the ozone dependence. This interference is part of the interference uncertainty listed in Table 3; the other part of the interference uncertainty is due to the pump which is discussed below. The method of standard additions can also be used to remove the artifact contribution to the signal if one assumes that the ambient mixing ratios are not changing over the calibration period. On an aircraft platform, particularly a rapidly moving one like the NASA DC-8, this assumption is often not valid.

The largest contributor to artifact formation from ozone in our system as deployed during TRACE-P was the rotor material in the VICI valves (Figure 1). The valve rotor material was Valcon E, a polyaryletherketone composite. Valcon R, a Teflon (PTFE) composite that is the most inert material available for VICI valves, has since replaced this material. No ozone interference was discernable in initial tests when using valves with this rotor material. There was no evidence of interference or artifact formation from nitrogen dioxide or sulfur dioxide for the FGCMS.

The KNF Teflon diaphragm pump was tested and shown to be an artifact source for acetaldehyde, propanal, butanal, and acetone. Again, no artifacts were observed for methanol, ethanol, or methyl ethyl ketone. As demonstrated in Figure 9, the artifact contribution to the signal increases as the pumping rate decreases. This indicates a relatively constant permeation from the pump of these compounds into the ambient air stream being pumped. Throughout the TRACE-P field program we recorded every five seconds all relevant instrument parameters, including the flow through the pump. Thus, as with ozone, we were able to remove the interference from this source for every data point. This assumed that the characteristics of the pump remained constant from the TRACE-P deployment through the testing period. As indicated earlier, a metal-bellows pump has since replaced the KNF pump. The new pump had not been evaluated fully at the time of manuscript preparation but initial experiments show virtually no artifact formation from ozone.

Results

The FGCMS operated smoothly and was remarkably robust. Data coverage was excellent and the system could operate continuously for more than 15 hours on a single liquid nitrogen charge of eight liters. As configured for TRACE-P, chromatograms of the target compounds were obtained every five minutes. However, the integrated sample collection time changed as a function of flow through the 1-liter sample holding volume (Figure 1). This, in turn, depended on altitude. The sample collection time ranged from about 15 seconds at the lowest altitudes (highest flow rates) to about one minute at the highest altitudes. Except for methanol, we found no evidence for a "memory effect" from sample to sample either during calibrations, ambient sampling, or post-mission testing. At very low flow rates (< 2 liters per minute) there was a memory effect on the order of 5% of the total signal on back-to-back runs, presumably due the

high polarity of this compound. We did not attempt to correct our data for this effect but this did increase the uncertainty for the methanol measurements from ±15% to ±20% (Table 3).

Figure 10 shows a typical example of a chromatogram obtained in flight (TRACE-P Flight 10). Shown are a subset of the compounds that were measured and the ion used for mass spectrometric quantification. Peak integration parameters were optimized for our chromatographic conditions and the data analysis was automated so that mixing ratios for the target compounds could be ascertained in near-real time and reported to the mission scientist. Before submission to the data archive, however, each chromatogram was carefully reintegrated.

Figure 11 shows results for a subset of measured compounds obtained for Flight 16 originating from Yokota Air Force base on March 29 (Greenwich mean time), 2001 targeting the sunrise chemistry of Asian outflow. The top panel shows results for the FGCMS aldehyde measurements along with formaldehyde measurements obtained by Fried et al. [this experiment] using a tunable laser diode technique. Superimposed on the data is a trace of the altitude profile. The bottom panel shows results for the FGCMS ketone measurements along with precursor hydrocarbon measurements obtained by Blake et al., [this experiment]. Vertical profiling showed a persistent polluted layer near the surface during this flight and a more polluted layer present at 2-3 km. These data demonstrate the utility of the instrument in observing a number of compounds simultaneously and that the instrument response was rapid enough to catch some but not all of the finer structure in the data as the 2-3 km plume was encountered. The data also reveal a shortcoming of the system as configured for TRACE-P. Note the absence of FGCMS data at the highest altitude leg of the flight for aldehydes. At these altitudes, the pumping capacity of our system was insufficient and precluded confidence in these data.

Figure 12 shows correlations during Flight 16 of carbon monoxide [Sachse et al., this experiment] with FGCMS-measured compounds acetone, methyl ethyl ketone, acetaldehyde, and propanal. This sortie was heavily impacted by Asian pollution sources and relatively good correlations might be expected and indeed, were observed ($r^2 > 0.6$ for all carbonyls). Similar correlations were observed when the sampled air masses were highly impacted from pollution. This gives an indication that the corrected FGCMS data is reasonable.

Figure 13 shows the FGCMS entire data set box and whisker plot of vertical profiles for acetaldehyde, methanol, acetone, propanal, butanal, and methyl ethyl ketone. The edges of the box are the 25^{th} and 75^{th} percentiles and the edges of the whisker line represent the 10^{th} and 90^{th}

percentiles. The median value is represented as a solid line. The tropospheric vertical profiles of propanal, butanal, and methyl ethyl ketone are the first to be reported in the literature. The aldehydes and methyl ethyl ketone show distinct profile trends with decreasing mixing ratios with altitude; these profiles would be expected of a shorter-lived compounds with higher surface or near-surface sources. Methanol and acetone profiles show less variability with altitude than the aldehydes as might be expected from these longer-lived compounds. In contrast with acetaldehyde, the methanol mixing ratio decreases at lower altitudes perhaps indicating that the ocean may be a sink for methanol. It is also likely that the data will discern whether mid-latitude Pacific Ocean is a sink or source of acetone as well, once low-level air-pollution events are accounted for. Large variations in mixing ratios of all compounds were observed during this experiment because polluted layers and biomass burning plumes were specifically targeted. A full treatment of the data will be presented in a future publication.

Conclusions

A fast GC-MS technique was developed through this proposal for NASA TRACE-P and deployed, measuring VOC species in-situ on the DC-8. The excellent data coverage obtained during this first deployment attests to the robustness of the instrument. Key features of the instrument are that it is sensitive enough to detect low pptv levels of all target analytes and it is extremely selective because target compounds are chromatographically separated and mass selected. Post-mission, the system was fully evaluated in the laboratory and some problems were uncovered with the Teflon diaphragm pump and the rotor material used in the VICI valves. The pump and rotor material have been replaced so that inert surfaces are present throughout the system. The TRACE-P experiment provided an excellent platform for the development and deployment of the FGCMS system and the feasibility of the instrument for in-situ measurements of carbonyl and alcohol species on an aircraft platform was demonstrated. Additional improvements in the system in terms of response time and the number of compounds measured are clearly achievable and will be the focus of future development.

From our work, it is clear that experimentalists need to exercise extreme care in the measurement of carbonyl species, particularly under clean-air conditions, because of the potential for artifact formation. Extensive testing of instruments for artifacts requires sophisticated equipment and is time-intensive. Before definitive arguments can be made on

budgets of carbonyl species and on the agreement between measurements and models, demonstration of artifact-free instrument operation is necessary.

References

Apel, E. C, D. D. Riemer, A. Hills, W. Baugh, J. Orlando, I. Faloona, D. Tan, W. Brune, B. Lamb, H. Westberg, M.A. Carroll, T. Thornberry, and C. Geron, Measurement and interpretation of isoprene fluxes, and isoprene, methacrolein, and methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 Intensive, *J. Geophys. Res.*, 107, No. D3, 10.1029, 2002.

Apel, E. C., J. G. Calvert, D. Riemer, W. Pos, R. Zika, T. Kleindienst, W. Lonneman, K. Fung, E. Fujita, P. Shepson, T. Starn, and P. T. Roberts, Measurements comparison of oxygenated volatile organic compounds at a rural site during the 1995 SOS Nashville Intensive, *J. Geophys. Res., 103*, 22,295-22,316, 1998.

Arnold, F., G. Knop, and H. Ziereis, Acetone measurements in the upper troposphere and lower stratosphere – implications for hydroxyl radical abundances, *Nature,* 321, 505, 1986.

Biesenthal, T., Q. Wu, P. Shepson, H. Wiebe, K. Anlauf and G. Mackay, A study of relationships between isoprene, its oxidation products, and ozone, in the lower Fraser Valley, BC, *Atmos. Environ.*, 31, 2049-2058, 1997.

Greenberg, J., A. Guenther, P. Zimmerman, W. Baugh, C. Geron, K. Davis, D. Helmig, and L. Klinger, Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer, *Atmos. Environ.*, 33, 855-867, 1999.

Goldan, P. D., W. C. Kuster, F. C. Fehsenfeld, S. A. Montzka, Hydrocarbon measurements in the southeastern United States: The Rural Oxidants in the Southern Environment (ROSE) program 1990, *J. Geophys. Res.*, 100, D12, 25945-25963, 1995.

Helmig D. and J. Greenberg, Automated in-situ gas chromatography/mass spectrometry (GC/MS) analysis of ppt level volatile organic trace gases using multistage solid adsorbent trapping, *J. Chrom. A,* 677, 123-132, 1994.

Helmig D., Review: Air Analysis by gas chromatography, *J. Chrom. A*, 843, 129-146, 1999.

Helmig D., J.Greenberg, A.Guenther, P. Zimmerman and C. Geron, Biogenic Volatile Organic Compound (BVOC) Emissions and their oxidation products at a temperate deciduous forest site, *J. Geophys. Res.* 103, 22397-22414, 1998.

Jaeglé, L.,D.J. Jacob, W.H. Brune, P. O. Wennberg, Chemistry of HOx radicals in the upper troposphere, *Atmos. Env.*, 35, 469-489, 2001.

Leibrock, E. and J. Slemr, Method for measurement of volatile oxygenated hydrocarbons in ambient air, *Atmos. Environ.* 31, 3329-3339, 1997.

Möhler, O, T. Reiner, and F. Arnold, A novel aircraft-based tandem mass spectrometer for atmospheric ion and trace gas measurements, *Rev. Sci. Instrum.*, 64, 1199, 1993.

Montzka, S.A., M. Trainer, P.D. Goldan, W.C. Kuster, and F.C. Fehsenfeld, Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere. *J. Geophys. Res.* 98, 1101-1111, 1993.

Montzka, S.A., M. Trainer, W. Angevine, and F.C. Fehsenfeld, Measurements of 3-methyl furan, methyl vinyl ketone, and methacrolein at a rural forested site in the southeastern United States, *J. Geophys. Res.* 100, 11393-11401, 1995.

Müller, J.F., and G. Brasseur, Sources of upper tropospheric HOx: A three-dimensional study, *J. Geophys. Res.*, 104, 1705-1715, 1999.

O'hara D., and H.B. Singh, Sensitive gas chromatographic detection of acetaldehyde and acetone using a reduction gas detector, *Atmos. Env.*, 22, 2613, 1988.

Rhoderick, G.C., and W.L Zielinski, Preparation of accurate multicomponent gas standards of volatile toxic organic compounds in the low-parts-per-billion range, *Anal. Chem.*, 60, 2454-2460, 1988.

Riemer, D., P. Willer, P. Milne, C. Farmer, R. Zika, E. Apel, K. Olszyna, T. Kliendienst, W. Lonneman, S. Bertman, P. Shepson and T. Starn, Observations of nonmethane hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern Untied States, *J. Geophys. Res.*, 103, 28,111-28,128, 1998.

Schade, G.W., A.H. Goldstein, D.W. Gray, and M.T. Lerdau, Canopy and leaf level 2-methyl-3-butene-2-ol fluxes from a ponderosa pine plantation, Atmospheric Environment, 34, 21, 3535-3544, 2000.

Singh, H. B. et al., Acetone in the atmosphere: distribution, sources and sinks, *J. Geophys. Res.*, 99, 1805-1819, 1994.

Singh, H. B., M. Kanakidou, P. Crutzen and D. Jacob, High concentrations and photochemistry of carbonyls and alcohols in the global troposphere, *Nature,* 378, 50-54, 1995.

Singh, H., Y. Chen, A. Tabazadeh, Y. Fukui, I. Bey, R. Yantosca, D. Jacob, F. Arnold, K. Wohlfrom, E. Atlas, F. Flocke, D. Blake, N. Blake, B. Heikes, J. Snow, R. Talbot, G. Gregory, G. Sachse, S. Vay, and Y. Kondo, Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic, *J. Geophys. Res.*, 105, 3795-3805, 2000.

Sprung, D., C. Jost, T. Reiner, A. Hansel, and A. Wisthaler, Airborne measurements of acetone and acetonitrile in the tropical Indian Ocean boundary layer and free troposphere: Aircraft-

based intercomparison of AP-CIMS and PTR-MS measurements, *J. Geophys. Res.* 106, 22, 28511-28528, 2001.

Sirju, A.-P. and P. B. Shepson, Laboratory and field investigation of the DNPH cartridge technique for the measurement of atmospheric carbonyl compounds, *Environ. Sci. Technol., 29*, 384-392, 1995.

Starn, T. K., P. B. Shepson, D. D. Riemer, R.G. Zika, and K. Olzyna, Nighttime isoprene chemistry at an urban-impacted forest site, J. *Geophys. Res.*, 103, D17, 22437-22447, 1998.

Warneke, C., R. Holzinger, A. Hansel, A. Jordan, and W. Lindinger, U. Pöschl, J. Williams, P. Hoor, H. Fischer, and P.J. Crutzen, H. A. Scheeren, J. Lelieveld, Isoprene and its oxidation products methyl vinyl ketone, methacrolein, and isoprene related peroxides measured on-line over a tropical rain forest in Suriname in March 1998, *J. Atmos. Chem.* 38, 167-185, 2001.

Wohlfrom, K.-H., T, Hauler, F. Arnold, and H. Singh, Acetone in the free troposphere and lower stratosphere: Aircraft-based CIMS and GC measurements over the North Atlantic and a first comparison, *Geophys. Res. Let.*, 26, 2849-2852, 1999.

Yokelson, R.J., J.G. Goode, D.E. Ward, R.A. Susott, R.E. Babbitt, D.D. Wade, I. Bertschi, W.M. Hao, and D.W.T. Griffith, Emissions of formaldehyde, acetic acid, methanol and other trace gases from biomass fires in North Carolina measured by airborne Fourier transform infrared spectroscopy (AFTIR), *J. Geophys. Res.* , 104, 30109, 1999.

Yokouchi, Y., Seasonal and diurnal variation of isoprene and its reaction products in a semirural area, *Atmos. Environ.*, 28, 16, 2651-2658, 1994.

Figure Captions

Figure 1. FGCMS inlet and plumbing diagram. See Experiment section B for discussion.

Figure 2. Dewar/preconcentraion system. The preconcentraion system consists of three traps. Trap 1 is a water removal trap held at –20 °C during sample load. Trap 2 is the enrichment trap held at –120 °C during sample load. Trap 3 is the cryofocuser trap held at –120 °C during transfer from the enrichment trap. Cooling is described in the text. Resistance heating is used for all three traps. Not shown are a heater, used to initially raise the headspace pressure, and a resistor network used to assess the liquid nitrogen level.

Figure 3. Simplified schema of the zero air generator/calibration system. See text for discussion.

Figure 4. GC-FID chromatogram of permeation tubes (top panel) and high-pressure cylinder with concentrations listed in table 2 (bottom panel). An HP-624 column (60 m, 0.25 mm I.D., 1.4 μ film thickness) was used in the analysis. The GC oven was held initially at 35 °C for two minutes, temperature programmed at a rate of 25 °C /min until the oven reached 190 °C and then held at 190 °C for 11 minutes giving a total chromatographic run time of 20 minutes. Carrier gas flowrate was maintained at 1.5 ml/min.

Figure 5. FGCMS instrument package. The individual components are described in the text.

Figure 6. Laboratory system used for instrument calibration and testing for interferences.

Figure 7. FGCMS calibration curves obtained for target compounds. Each data point represents the average of 5 measurements. The vertical bars represent the standard deviation for the 5 measurements.

Figure 8. Results from interference testing with ozone. Methyl ethyl ketone, methanol, and ethanol showed no response to ozone. Each data point represents the average of six measurements obtained on two separate days. The vertical bars indicate the standard deviation of the six measurements.

Figure 9. Results of tests showing the artifact produced from the pump used during the TRACE-P experiments. As the pumping rate decreased the relative artifact contribution increased. Methyl ethyl ketone, methanol, and ethanol showed no pump artifacts. Each data point represents the

average of 6 measurements obtained on two separate days. The vertical bars indicate the standard deviation of the 6 measurements.

Figure 10. Typical chromatogram, obtained during the TRACE-P mission, of a subset of the targeted compounds. Ions used for quantification for individual compounds are color-coded.

Figure 11. Results from TRACE-P flight 16 for the FGCMS measured carbonyls. The top panel shows the aldehydes measured along with the tunable diode laser measurements of formaldehyde [Fired et al., this experiment]. The bottom panel shows the ketones, acetone, and MEK, along with hydrocarbon precursor compounds [Blake et al., this experiment].

Figure 12. Correlations of carbon monoxide with measured ketones and aldehydes for flight 16.

Figure 13. Box and whisker vertical profile plots of acetaldehyde, methanol, and acetone measured by the FGCMS. See text for discussion.

Table 1. Standard used during TRACE-P (NASA A)

Compound	High Pressure Cylinder gravimetric (ppbv) Pre-mission values	% Difference Analysis of mean values* Post-mission/Pre-mission
Methanol	394 ± 15	-7
Ethanol	48 ± 3	2
Acetone	554 ± 12	-2
MEK	53 ± 3	-2
Acetaldehyde	98 ± 3	-9
Propanal	48 ± 2	2
Butanal	9.6 ± 0.5	-3
Carbon tetrachloride	4.2 ± 0.1	1

*Analysis based on relative calibration factors from FID and represent an average of three chromatographic runs.

Table 2. Quantification of standards results

Compound	High Pressure Cylinder gravimetric (ppmv)	High Pressure Cylinder analyzed (ppmv)*	FTIR (ppmv)
Methanol	3.00 ± 0.03	3.0 ± 0.1	2.9 ± 0.2
Ethanol	3.02 ± 0.03	n.d.	2.9 ± 0.3
Acetone	3.03 ± 0.03	3.03 ± 0.08	3.2 ± 0.2
MEK	3.04 ± 0.03	n.d	2.5 ± 0.3
Acetaldehyde	3.03 ± 0.03	n.d	3.2 ± 0.4
Propanal	3.03 ± 0.03	n.d	n.d.
Butanal	3.02 ± 0.03	n.d	n.d.

*Analysis based on calibration factors from permeation tubes.
n.d. - not determined

Table 3. FGCMS detection limits and derived uncertainties during TRACE-P.

Compound	Limit of detection (pptv)	Interference uncertainty (pptv)	Instrumental uncertainty	Total measurement uncertainty
Methanol	50	0	± 20%	± 20%
Acetone	75	± 75	± 15%	± (15 + (75/[ ]*100))%
MEK	5	0	± 15%	± 15%
Acetaldehyde	70	± 70	± 15%	± (15 + (70/[ ]*100))%
Propanal	30	± 30	± 15%	± (15 + (30/[ ]*100))%
Butanal	12	± 12	± 15%	± (15 + (12/[ ]*100))%
Carbon tetrachloride	1	0	± 5%	± 5%

*Detection limits determined as five times the baseline noise. Interference uncertainty was determined by the laboratory derived interference effects due to ozone and pump interference on the signal at the 2σ confidence level. Instrumental uncertainty is determined from the error propagation of accuracy and precision; the accuracy is a function of the standards, flow controller calibration and uncertainty of the sampled volume; the precision is a function of the reproducibility of the signal when no interference is present. The total measurement uncertainty is a combination of the interference uncertainty and the instrumental uncertainty.

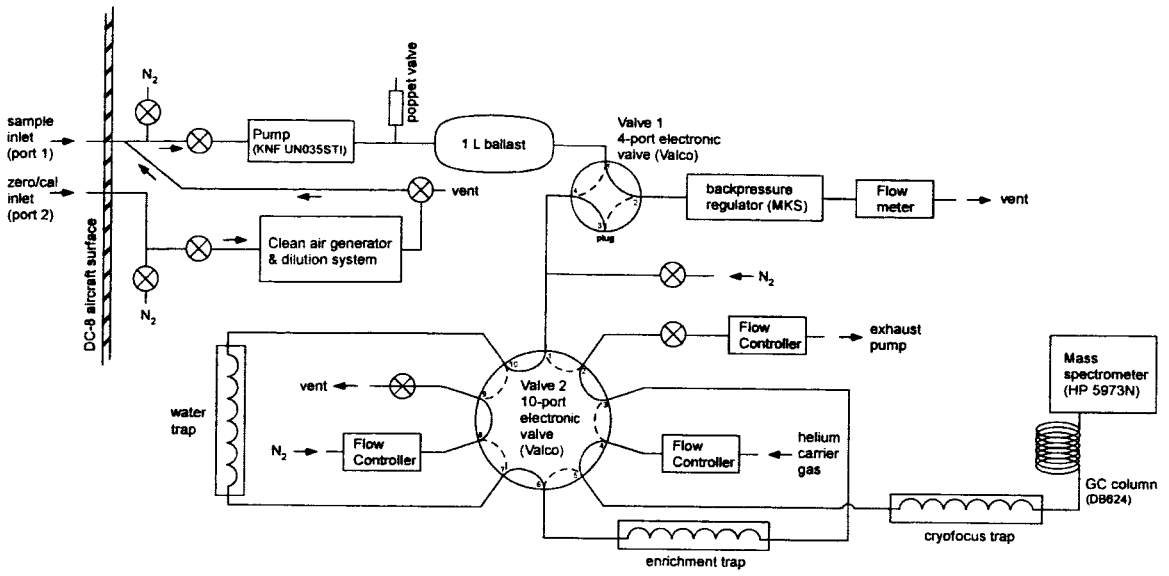

sample inlet (port 1)
zero/cal inlet (port 2)
DC-8 aircraft surface
N2
Pump (KNF UN035STI)
poppet valve
1 L ballast
Valve 1 4-port electronic valve (Valco)
vent
Clean air generator & dilution system
backpressure regulator (MKS)
Flow meter
vent
plug
N2
Flow Controller
exhaust pump
Mass spectrometer (HP 5973N)
water trap
vent
Valve 2 10-port electronic valve (Valco)
N2
Flow Controller
Flow Controller
helium carrier gas
GC column (DB624)
cryofocus trap
enrichment trap

Figure 1.

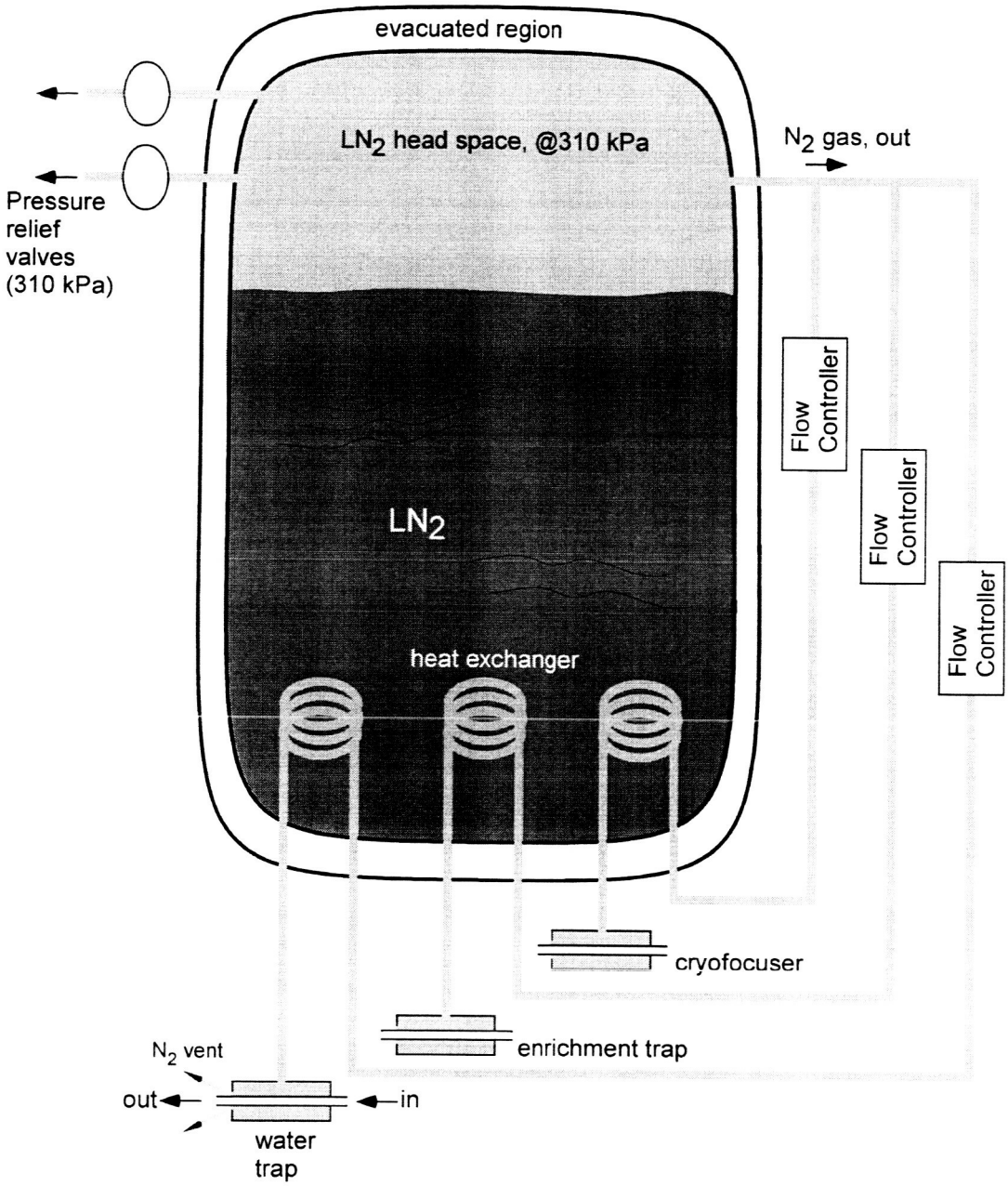

evacuated region
LN_2 head space, @310 kPa
N_2 gas, out
Pressure relief valves (310 kPa)
Flow Controller
Flow Controller
Flow Controller
LN_2
heat exchanger
cryofocuser
enrichment trap
N_2 vent
out
in
water trap

Figure 2.

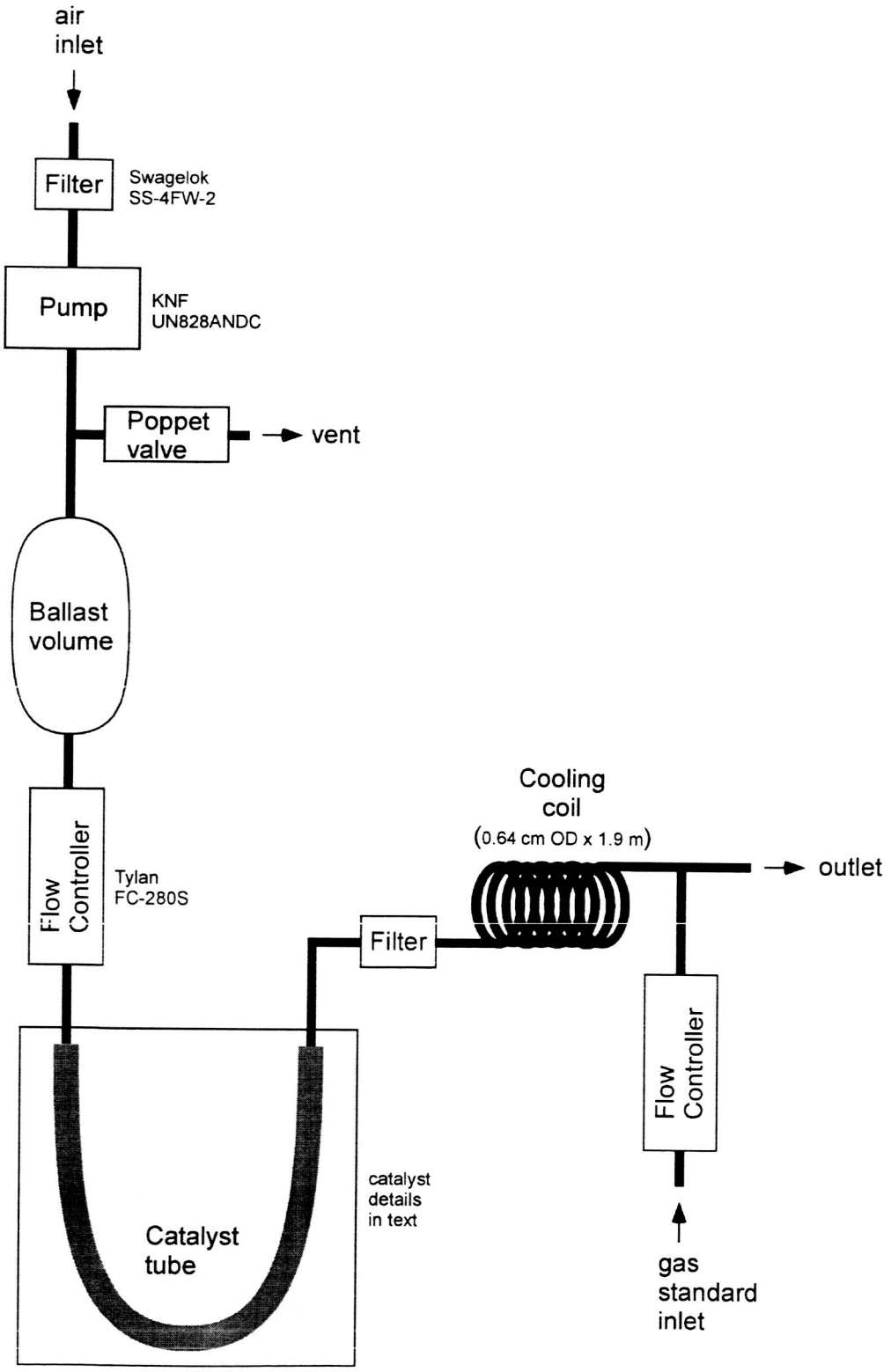

air
inlet
Filter
Swagelok
SS-4FW-2
Pump
KNF
UN828ANDC
Poppet
valve
vent
Ballast
volume
Flow
Controller
Tylan
FC-280S
Cooling
coil
(0.64 cm OD x 1.9 m)
outlet
Filter
Flow
Controller
catalyst
details
in text
Catalyst
tube
gas
standard
inlet

Figure 3.

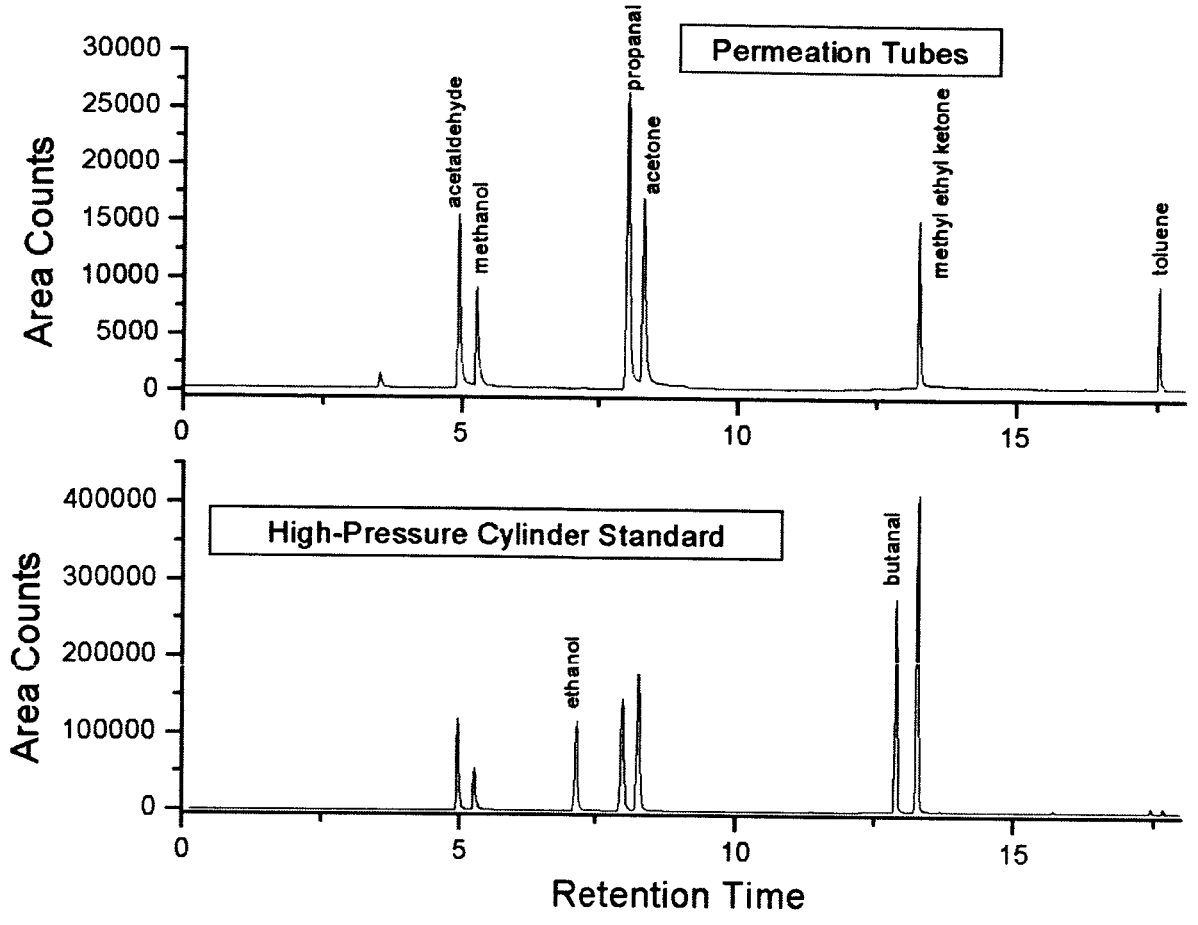

Permeation Tubes
acetaldehyde
methanol
propanal
acetone
methyl ethyl ketone
toluene
Area Counts
30000
25000
20000
15000
10000
5000
0
0
5
10
15
High-Pressure Cylinder Standard
ethanol
butanal
Area Counts
400000
300000
200000
100000
0
0
5
10
15
Retention Time

Figure 4.

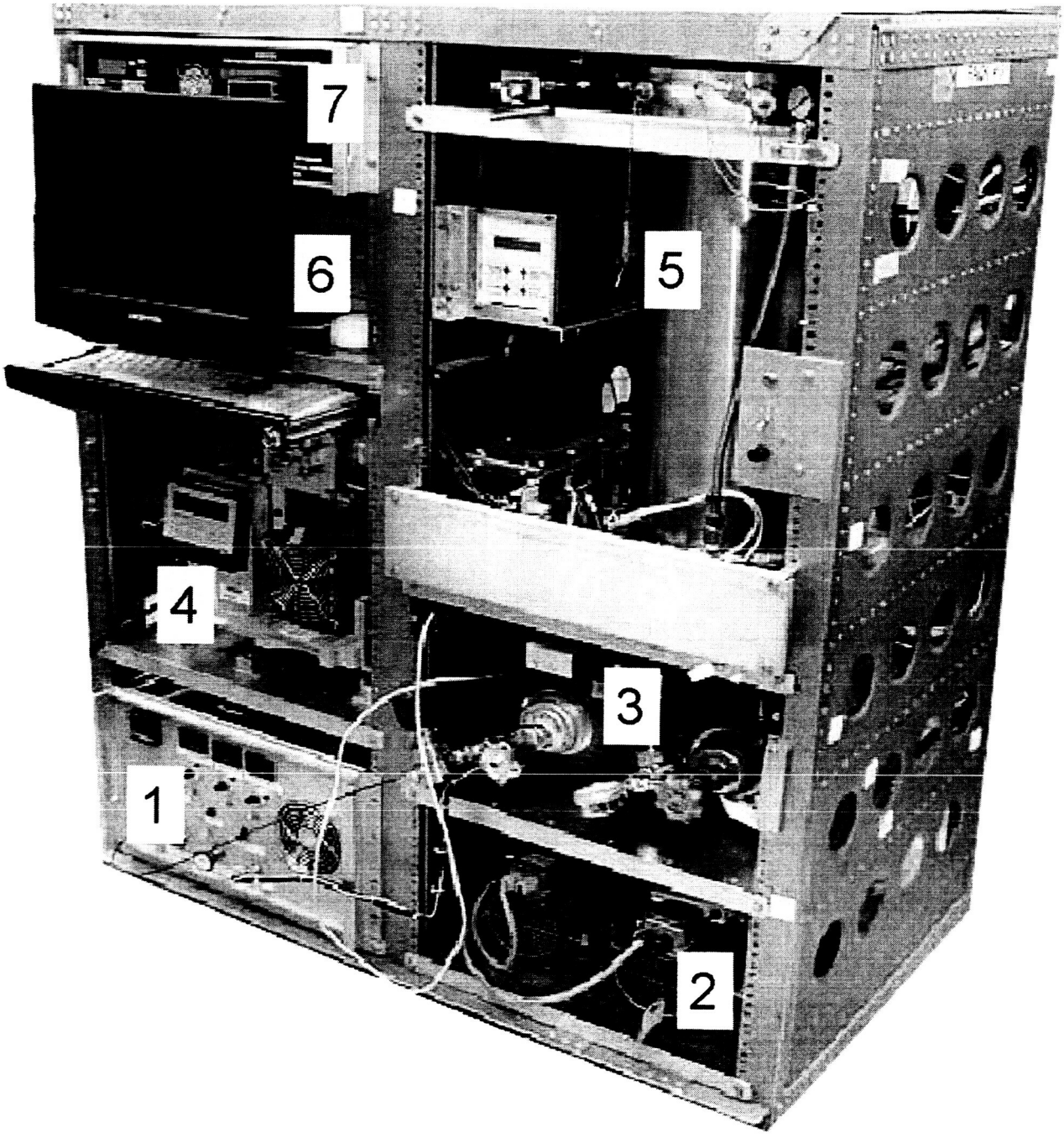


Figure 5.

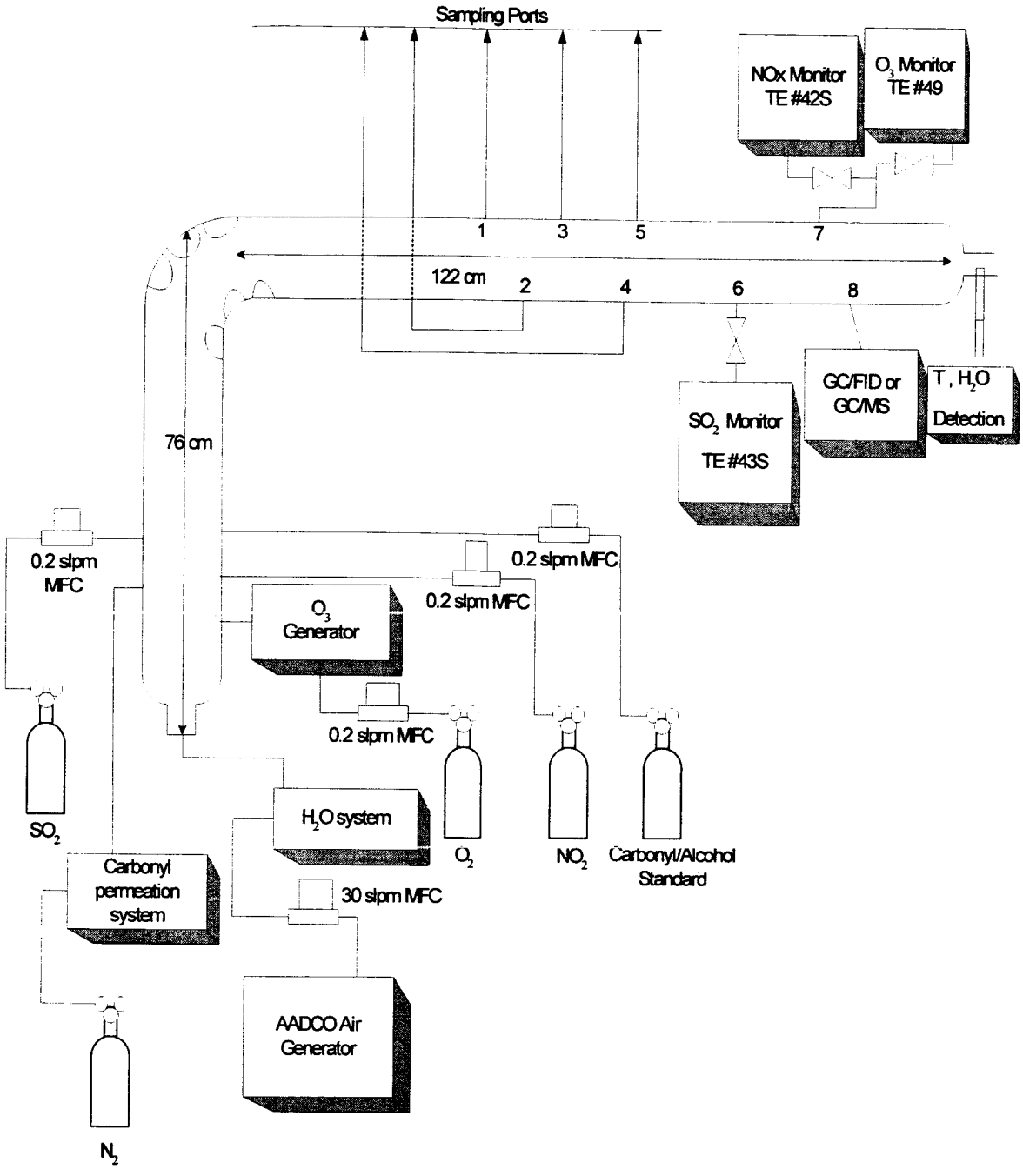

Sampling Ports
NOx Monitor TE #42S
O_3 Monitor TE #49
1
3
5
7
122 cm
2
4
6
8
SO_2 Monitor TE #43S
GC/FID or GC/MS
T, H_2O Detection
76 cm
0.2 slpm MFC
0.2 slpm MFC
0.2 slpm MFC
O_3 Generator
0.2 slpm MFC
SO_2
H_2O system
O_2
NO_2
Carbonyl/Alcohol Standard
Carbonyl permeation system
30 slpm MFC
AADCO Air Generator
N_2

Figure 6.

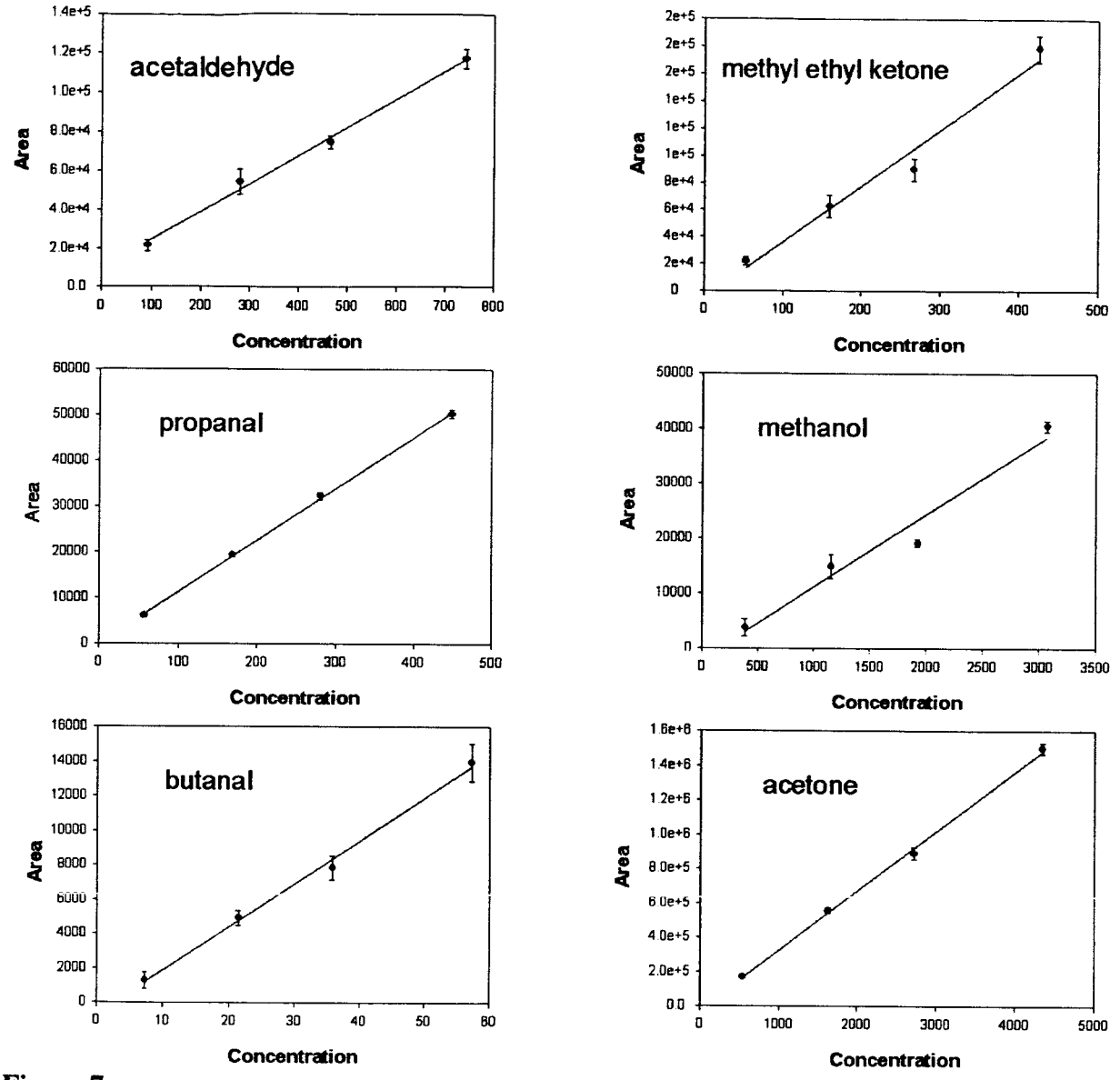

acetaldehyde
Area
Concentration
methyl ethyl ketone
Area
Concentration
propanal
Area
Concentration
methanol
Area
Concentration
butanal
Area
Concentration
acetone
Area
Concentration

Figure 7.

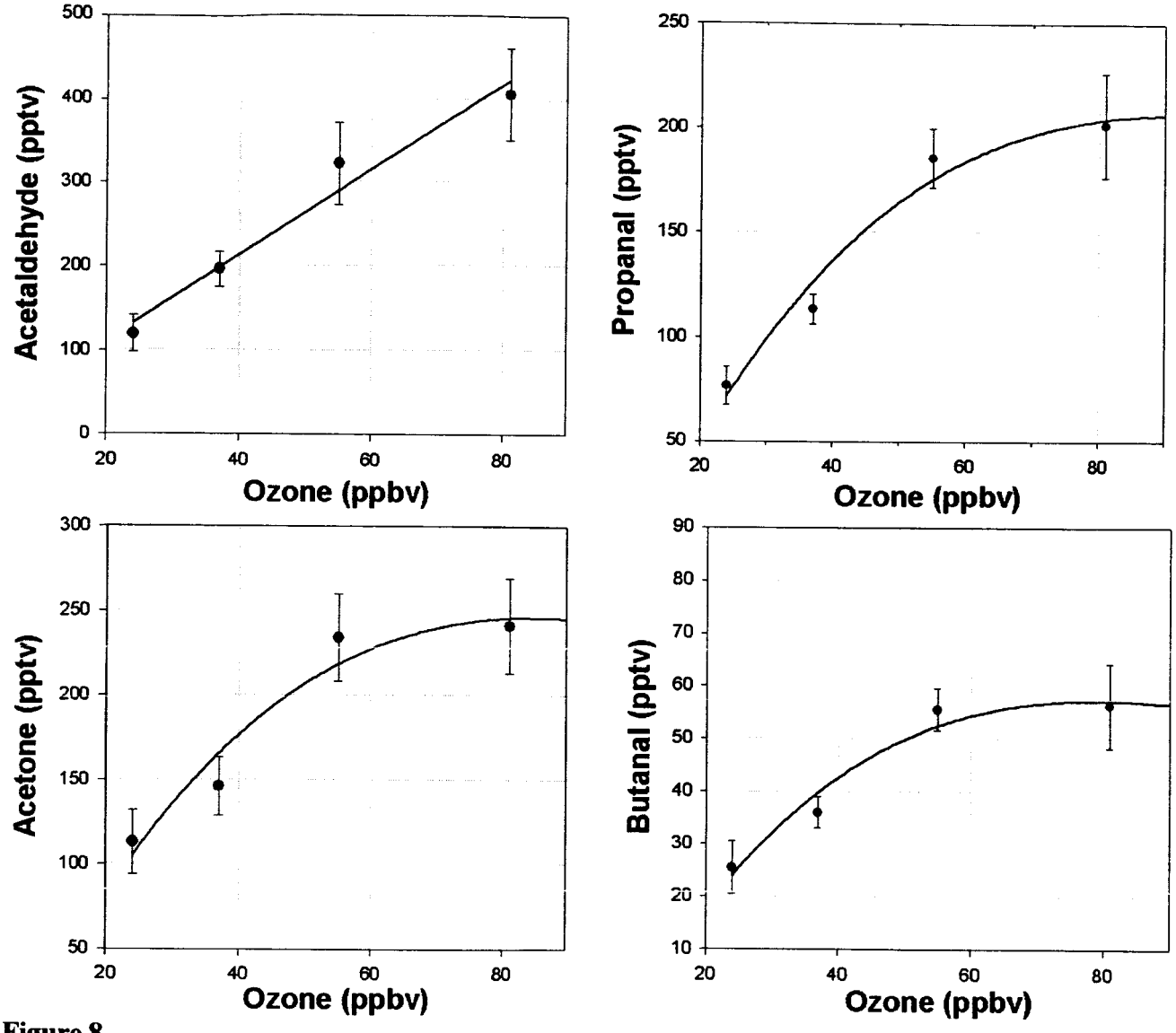

Acetaldehyde (pptv)
Ozone (ppbv)
Propanal (pptv)
Ozone (ppbv)
Acetone (pptv)
Ozone (ppbv)
Butanal (pptv)
Ozone (ppbv)

Figure 8.

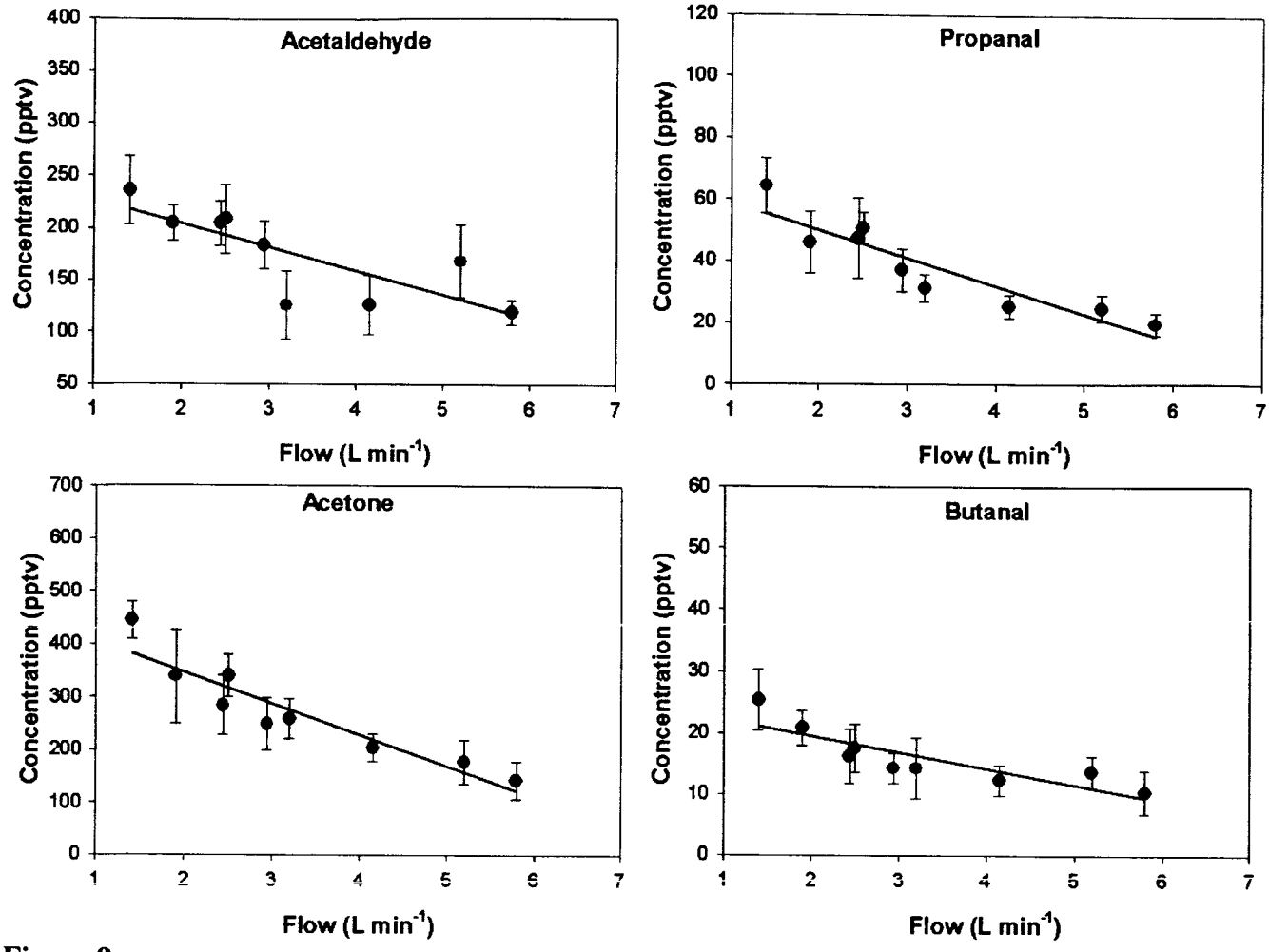

Acetaldehyde
Concentration (pptv)
Flow (L min-1)
Propanal
Concentration (pptv)
Flow (L min-1)
Acetone
Concentration (pptv)
Flow (L min-1)
Butanal
Concentration (pptv)
Flow (L min-1)

Figure 9.

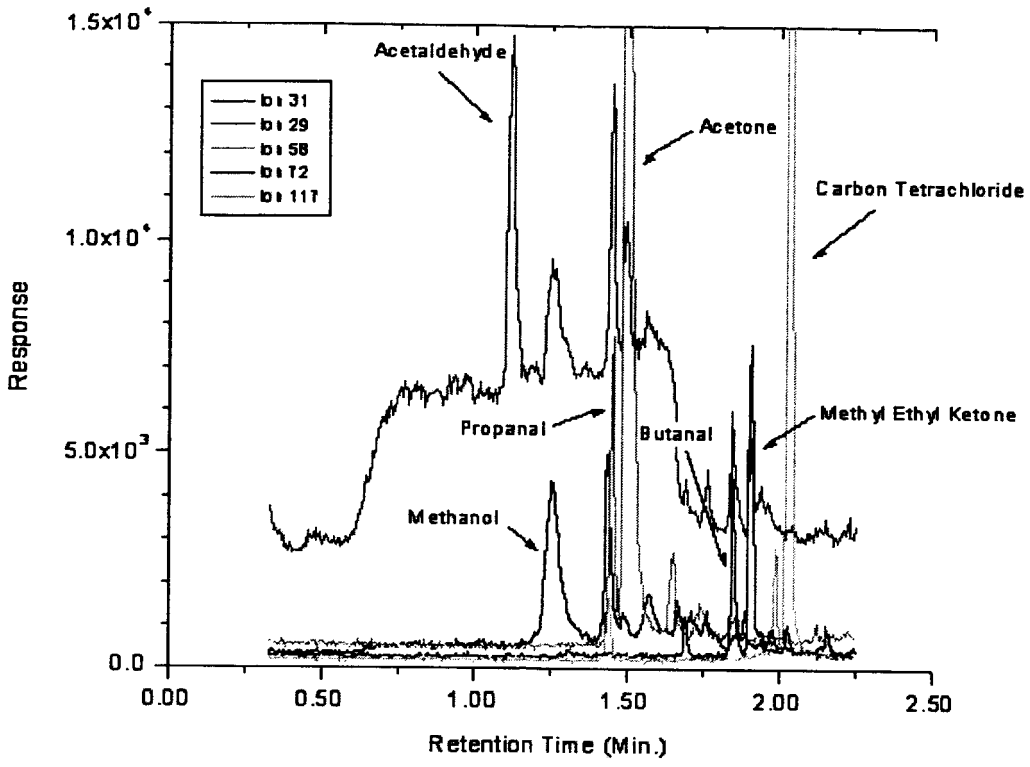

1.5x10⁴
1.0x10⁴
5.0x10³
0.0
Response
0.00
0.50
1.00
1.50
2.00
2.50
Retention Time (Min.)
Acetaldehyde
Acetone
Carbon Tetrachloride
Propanal
Butanal
Methyl Ethyl Ketone
Methanol

Figure 10.

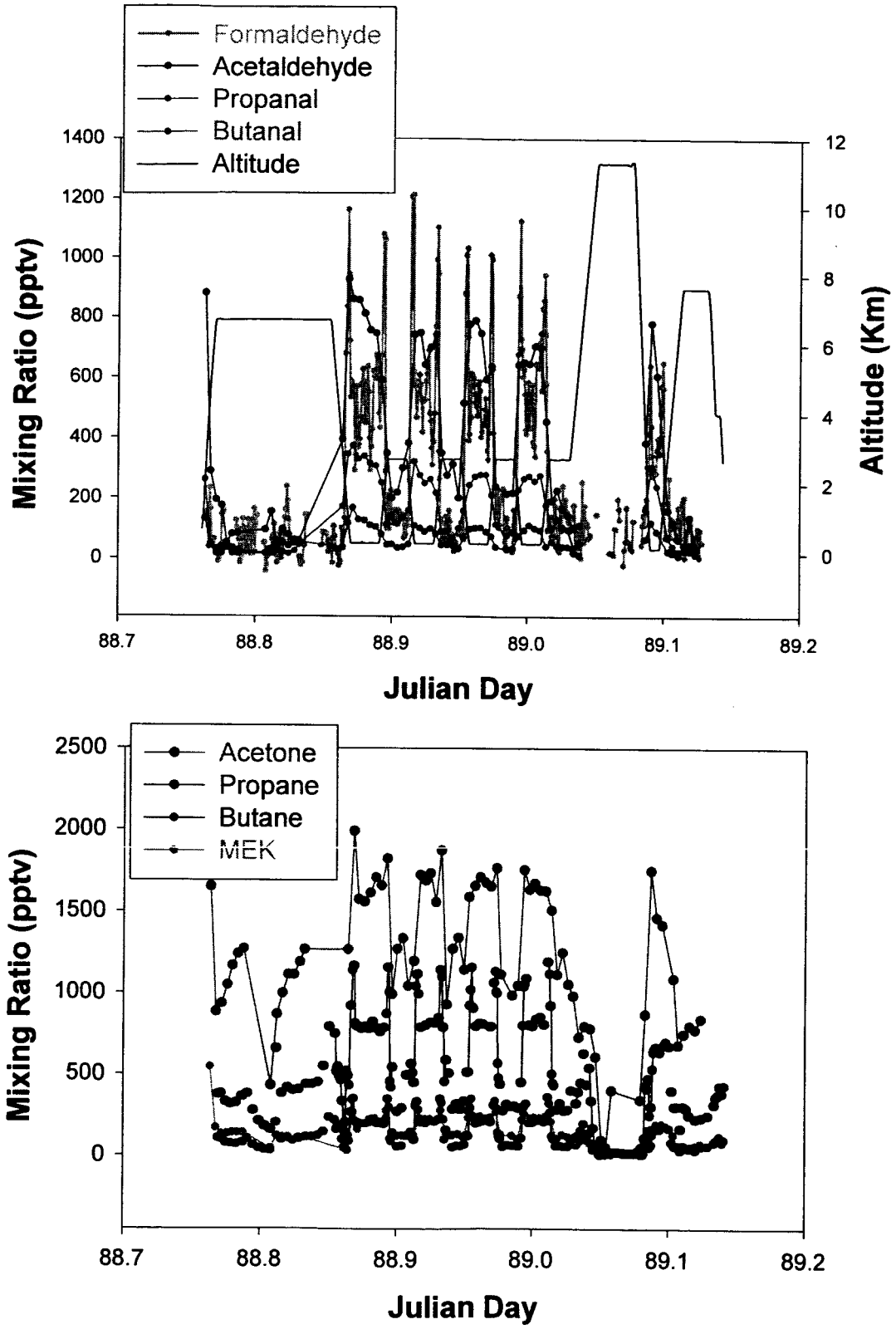
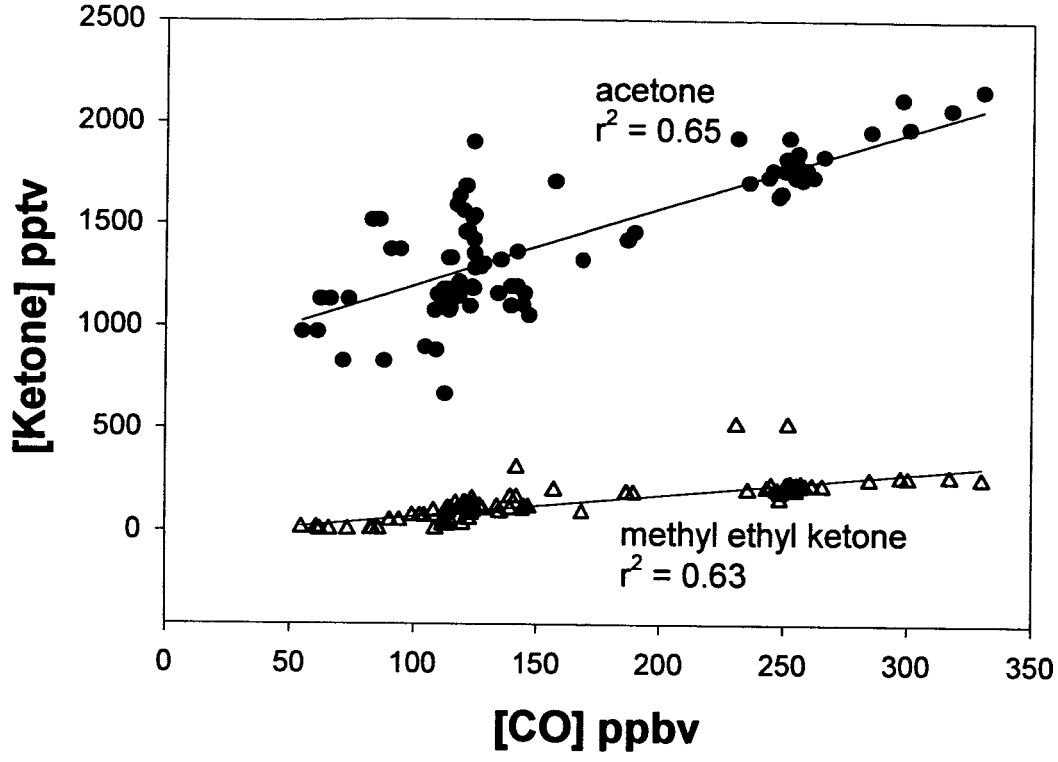

Formaldehyde
Acetaldehyde
Propanal
Butanal
Altitude
Mixing Ratio (pptv)
Altitude (Km)
Julian Day
Acetone
Propane
Butane
MEK
Mixing Ratio (pptv)
Julian Day

Figure 11.


2500
2000
1500
1000
500
0
[Ketone] pptv
acetone
r2 = 0.65
methyl ethyl ketone
r2 = 0.63
0
50
100
150
200
250
300
350
[CO] ppbv

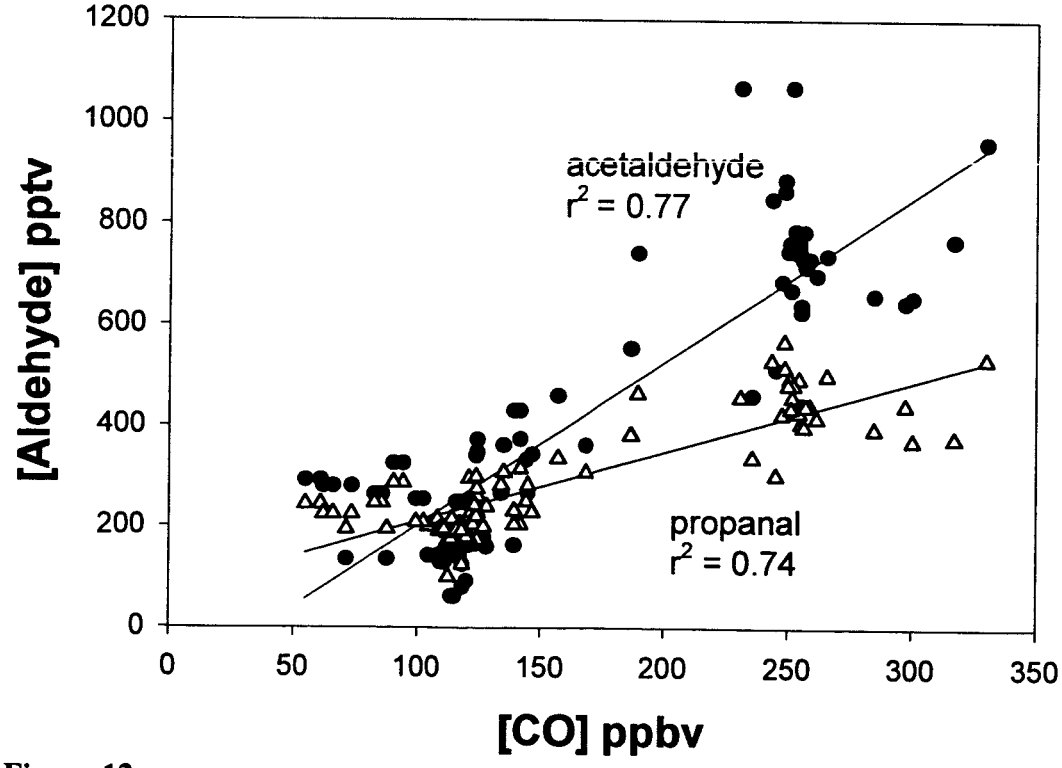
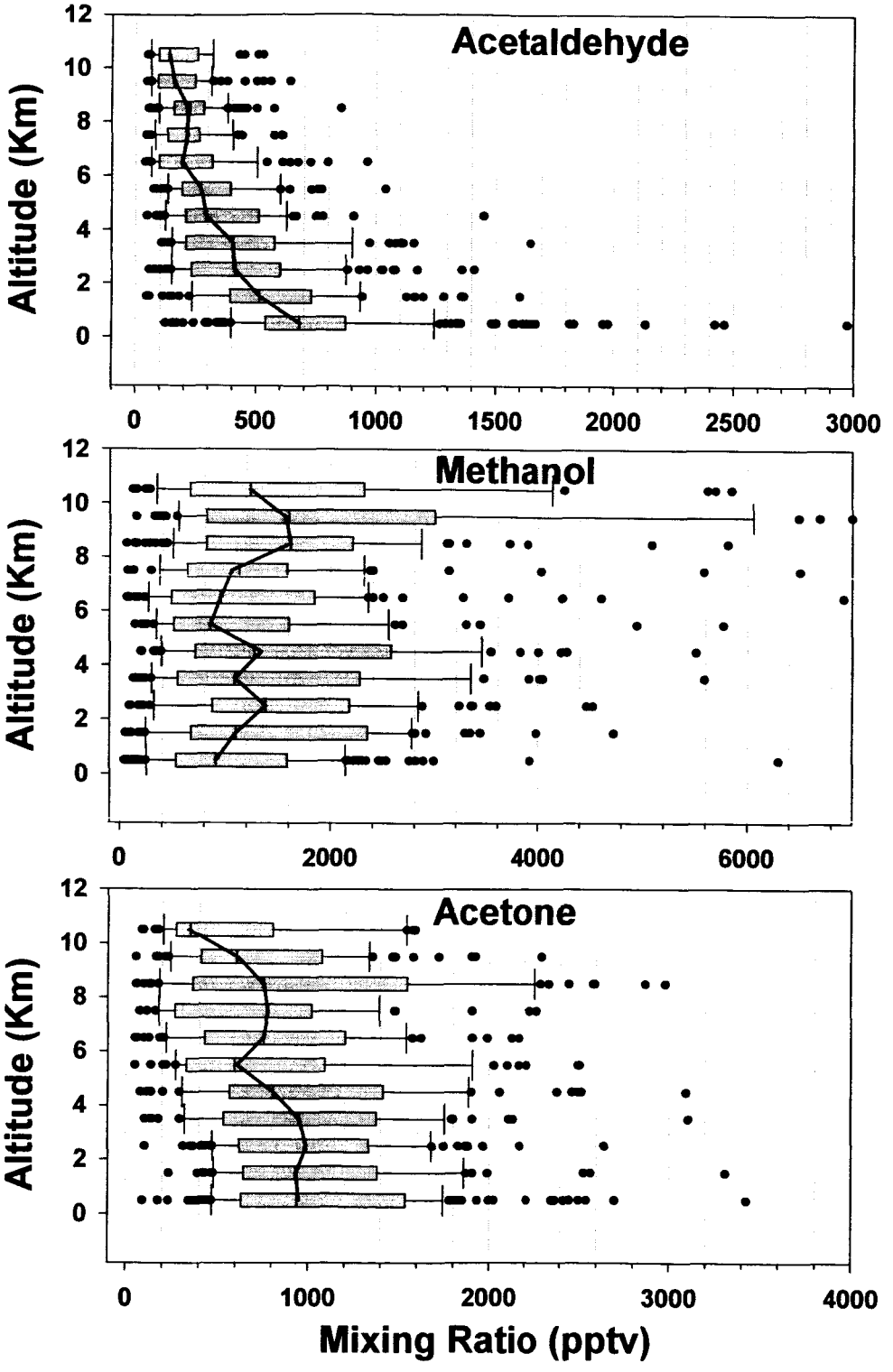

1200
1000
800
600
400
200
0
[Aldehyde] pptv
acetaldehyde
r2 = 0.77
propanal
r2 = 0.74
0
50
100
150
200
250
300
350
[CO] ppbv

Figure 12.


Acetaldehyde
Methanol
Acetone
Altitude (Km)
Mixing Ratio (pptv)
0
2
4
6
8
10
12
0
500
1000
1500
2000
2500
3000
0
2000
4000
6000
0
1000
2000
3000
4000

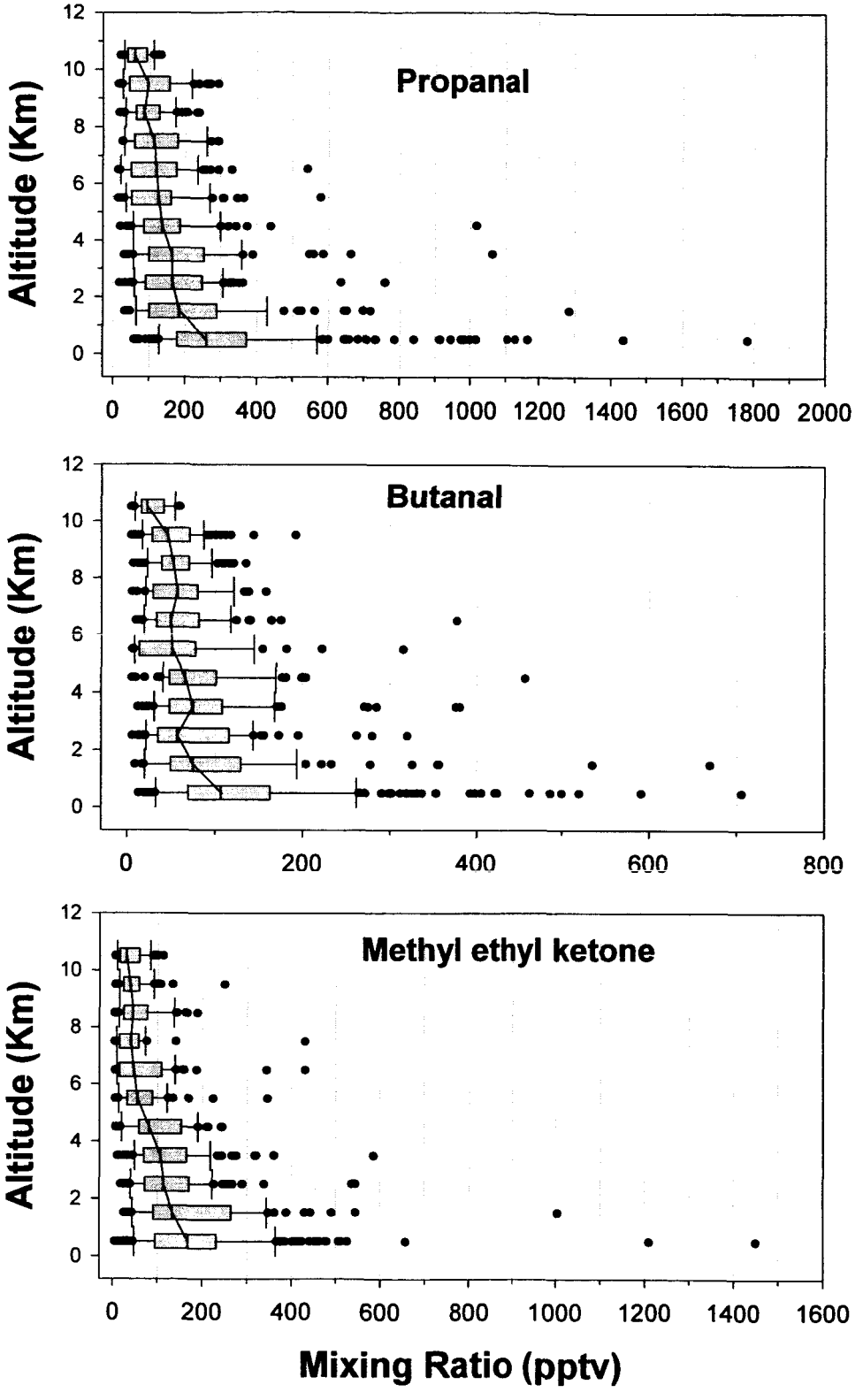

Propanal
Butanal
Methyl ethyl ketone
Altitude (Km)
Mixing Ratio (pptv)

Figure 13.