

Measurements of alcohols, aldehydes and ketones during TRACE-P

E. C. Apel, A. Hills, R. Lueb, A. Fried, NCAR, Boulder, CO, D. D. Riemer, University of Miami, Miami, FL, H. B. Singh, NASA Ames, Moffett Field, CA, G. Sachse, J. Crawford, NASA Langley, Hampton, VA, D. R. Blake, UCI, Irvine, CA.

Introduction

We developed a fast response gas chromatograph/mass spectrometer (FGCMS) instrument to measure $\leq C_6$ carbonyl compounds, methanol and ethanol (OVOCs) aboard aircraft. The time response for the measurement of these compounds for the TRACE-P mission was 5 minutes but this can be improved substantially. The system consists of 4 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 custom-built compact GC that can be temperature programmed and rapidly cooled. Detection is accomplished with an Agilent Technologies 5973 mass selective detector. Air samples are drawn into the introduction system where water removal and pre-concentration occur. Helium carrier gas rapidly transfers the preconcentrated compounds to the custom GC fitted with an HP-624 column. The carbonyl and alcohol compounds of interest elute rapidly from the column and into the mass spectrometer operating in the single ion mode. This method provides unambiguous identification because the compounds are chromatographically separated and mass selected. The sensitivity as currently configured is estimated to be between 2 and 10 pptv depending on the compound. The instrument package consumes less than 2000W of power, and is fully automated with LabView™. We have developed methods for producing highly accurate gas phase standards for the compounds of interest and for testing for interferences.

The FGCMS was deployed on the highly instrumented NASA DC-8 aircraft during the TRACE-P mission. With this new instrument we obtained data for 15 out of 17 mission flights. A wide variety of air masses were sampled during the mission; highly polluted as well as clean air masses were encountered. Key marker compounds measured by other research groups indicated characteristic biomass burning and industrial pollution plumes which are also reflected in the OVOC measurements. Not surprisingly, dramatic differences were observed in the mixing ratios and vertical profiles of the longer-lived species, acetone and methanol, compared to the shorter-lived species (methyl ethyl ketone and the aldehydes). Higher than predicted abundances of acetaldehyde, propanal and butanal were observed by both the FGCMS and the instrument deployed on the same aircraft by Dr. Hanwant Singh (NASA Ames) which suggests sources other than hydrocarbon oxidation.

FGCMS Instrument

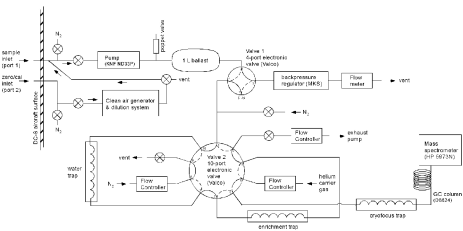
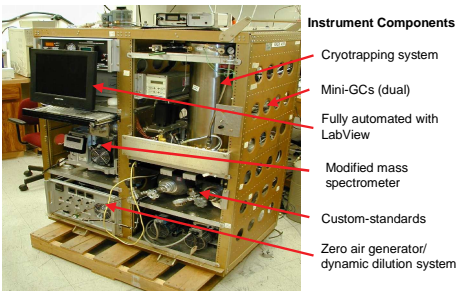


Figure 1. FGCMS Inlet and plumbing system. Silonite™ (Entech Instruments, fused silica lined stainless steel tubing) was used for the entire inlet line. Zeroing the inlet was accomplished by scrubbing ambient air (see Figures 2b, 3) and overflowing the inlet with the return air. Calibration was performed by adding standards to the scrubbed air and returning the flow to the inlet.

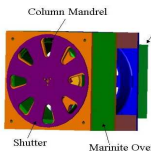


Figure 2a. Custom-built gas chromatograph

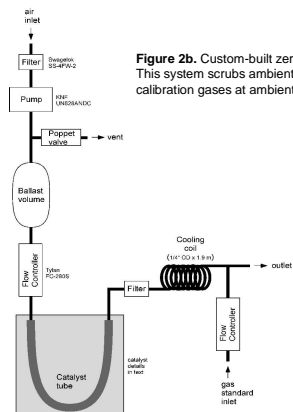


Figure 2b. Custom-built zero-air/calibration system. This system scrubs ambient air and produces diluted calibration gases at ambient humidity.

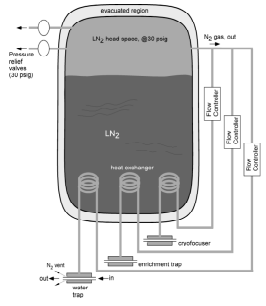


Figure 2c. Custom-built dewar used as the basis for the preconcentration system. Nitrogen gas is circulated through the coils shown here which, in practice, are immersed in liquid nitrogen. The cooled nitrogen gas is then used to rapidly cool the water trap, sample trap, and cryofocusing trap.

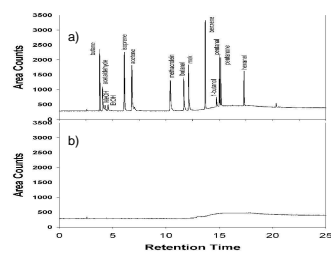


Figure 3. Demonstration of the effectiveness of the on-board zero air generator. Mixing ratios of the named compounds in the prepared mixture in (a) are between 3 and 10 pptv. This same air mixture is passed through the zero air generator in (b) and all compounds are scrubbed to less than 10 pptv.

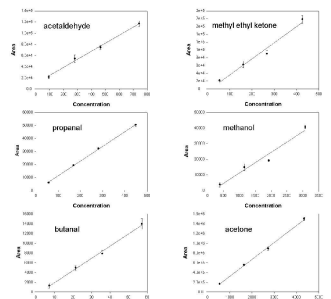


Figure 4. Post flight calibration curves. Five measurements were taken for each data point. The error bars represent the standard deviation of the measurements.

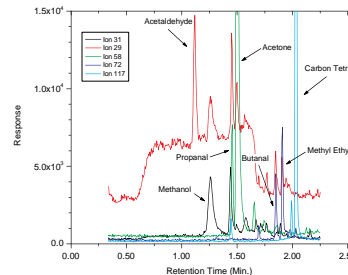


Figure 5. Typical chromatogram obtained during the mission of a subset of the targeted compounds.

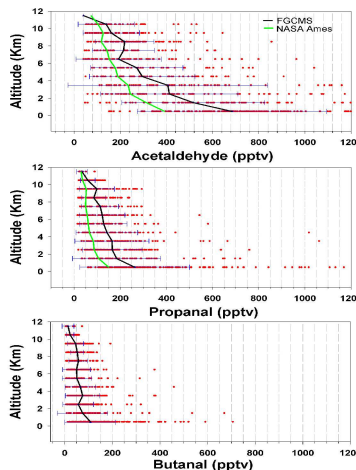


Figure 6. Vertical profiles and median mixing ratios of the measured aldehydes shown for every 1 km of vertical altitude. The red dots represent all the FGCMS data collected in the given altitude bin and the bars represent one standard deviation. The black line runs through the FGCMS median mixing ratios. The green line runs through binned (1km) median mixing ratios of the NASA Ames data and has been adjusted to the NCAR calibration. See discussion section for further details.

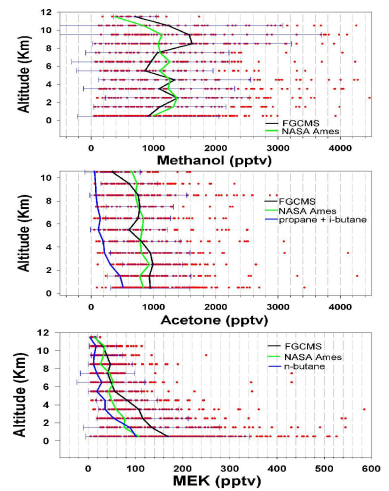


Figure 7. Vertical profiles and median mixing ratios of the measured named compounds shown for every 1 km of vertical altitude. The red dots represent all the FGCMS data collected in the given altitude bin and the bars represent one standard deviation. The black line runs through the FGCMS median mixing ratios. The green line runs through binned (1km) median mixing ratios of the NASA Ames data and has been adjusted to the NCAR calibration. The dark blue line runs through the binned (1km) UCI hydrocarbon data. Propane and i-butane are the major hydrocarbon precursors to acetone and n-butane is the major precursor to methyl ethyl ketone.

Biomass Burning: Evidence of methanol as a major emission

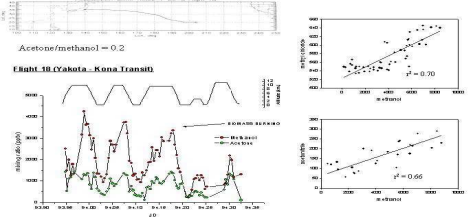


Figure 8. Biomass burning plume encountered during flight 18. Note the enhanced concentrations of acetone and especially methanol. Good correlations are observed between methanol and methyl chloride and acetonitrile indicating a common source.

Discussion

During TRACE-P, the disparity between modeled aldehydes, using only known hydrocarbon precursors as the aldehyde source, and measured aldehydes was found to be more significant in clean tropospheric air than in polluted air and was larger for the FGCMS data than for the NASA Ames data. This suggests additional aldehyde sources not included in the models. To qualitatively reconcile the model-measurement differences, both a primary surface emission source must be invoked as well as an additional source in the middle to upper troposphere. Figure 10 below explores the potential role of the ocean in providing these sources.

ROLE OF OCEAN IN ATMOSPHERIC BUDGETS OF OVOCs

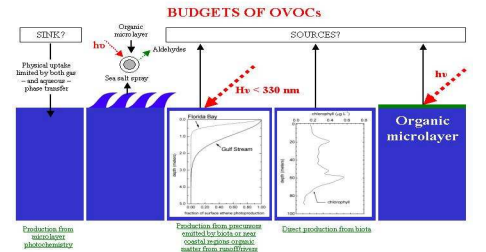


Figure 10. Ocean atmosphere interactions and potential formation mechanisms for oxygenated compounds in the marine boundary layer and the remote atmosphere.

Conclusions

A fast gas chromatograph mass spectrometric (FGCMS) system was successfully developed and deployed during TRACE-P.

Comparisons of measurements with the NASA Ames instrument were better for the longer-lived species (methanol, acetone) than for the shorter-lived aldehydes and methyl ethyl ketone.

Data suggests significant sources (other than hydrocarbon oxidation) for acetone and methyl ethyl ketone. For acetone, this is in accord with known source estimates.

Higher than predicted aldehyde mixing ratios were observed and exacerbated in clean air. Possible mechanisms involving the ocean may explain the differences.