

COMPACT, AUTONOMOUS WHOLE AIR SAMPLER FOR TRACE GAS STUDIES ABOARD THE SOFIA AIRCRAFT

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ABSTRACT

We propose to use an advanced, new-generation air sampler for trace gas studies aboard the NASA-Ames based Stratospheric Observatory for Infrared Astronomy (SOFIA) 747 aircraft. The sampler allows for the autonomous collection of up to 50 whole air samples per flight, to be analyzed for a wide range of trace gas components including hydrocarbons, halocarbons, sulfur compounds, and organic nitrates. These compounds play key roles in the chemistry and physics of the atmosphere, including stratospheric ozone (O₃) depletion, tropospheric O₃ formation, radiative forcing, and the oxidative capacity of the atmosphere. In addition, trace gas measurements from whole air samples provide detailed information on air mass sources, transport, and photochemical processing that is useful to atmospheric chemistry and dynamics investigations. SOFIA provides an excellent opportunity for regular, long-term (20-year) airborne monitoring of important trace gases that impact global change, in particular chlorofluorocarbons (CFCs) and their replacements, halons (e.g. H-1211), hydrocarbons (e.g. ethane, propane, *n*-butane), dimethyl sulfide (DMS), and methyl bromide (CH₃Br).

The sampler design draws on years of successful experience of the principal investigator in whole air sampling aboard a large variety of research aircraft. The sampler will be modular, so it will be possible to sample trace gases with minimal handling requirements by personnel in the field. Further, the sampler is adaptable for specialized flasks, if required. The sampler design takes advantage of advances in analytical procedures for trace gas studies. Small volume samples are collected that will be analyzed using new high-sensitivity mass spectrometric techniques, or with improvements to existing technology. The use of smaller sample collection vessels leads to a more compact and lighter weight system than previous airborne versions. A versatile computer control system has the ability to be pre-programmed for completely automated operation, or sample commands may be given by an on-board operator to sample special features. As with past instruments designed by our group, only high-purity, elastomer-free component materials are used for sample collection, to ensure artifact-free sampling for the widest range of trace gas species.

WHOLE AIR SAMPLING: IMPORTANCE AND RESEARCH OBJECTIVES

Halocarbons and nonmethane hydrocarbons (NMHCs) are among the most important classes of trace molecules in the atmosphere. Very long-lived halocarbons are linked to stratospheric ozone (O₃) depletion and greenhouse forcing, while NMHCs directly influence the oxidative capacity of the atmosphere and participate as short-lived tropospheric O₃ precursors. Other notable atmospheric species include methyl bromide (CH₃Br), an important ozone-depleting gas, and dimethyl sulfide (DMS), involved in the formation of cloud condensation nuclei. The unique contribution of whole air sampling to air chemistry and dynamics missions is related to the large and diverse range of trace gases that can be measured from whole air samples (a selected subset of trace gases commonly measured from whole air sampling is listed in Table 1). Examples of tropospheric and stratospheric processes that have been examined using ground-based and airborne whole air sampling include:

- characterization of rural and urban oxidant and aerosol formation (e.g. *Blake and Rowland*, 1995; *Chen et al.*, 2001; *Katzenstein et al.*, 2003, *Ryerson et al.*, 2003)
- impact of biomass burning emissions on global atmospheric chemistry (e.g. *Blake et al.*, 1994, 1999)
- examination of continental outflow from East Asia (e.g. *Blake et al.*, 2003)
- long-term monitoring of tropospheric hydrocarbon and halocarbon levels (e.g. *Simpson et al.*, 2002, 2004)
- studies of convective redistribution of reactive gases (e.g. *Ridley et al.*, 2004)
- investigation of heterogeneous chlorine activation in the upper troposphere (e.g. *Simpson et al.*, 2003)
- evaluation of stratosphere/troposphere exchange processes (e.g. *Flocke et al.*, 1999)
- determination of halogen budgets in the troposphere and stratosphere (e.g. *Schaffler et al.*, 1999, 2003).

Whole air sampling for the atmospheric chemistry community is expected to remain a high priority well into the future. For example, our current investigations show that CFCs continue to be released within countries such as China, and the long-term monitoring of CFCs and their replacements remains a high priority during the next couple of decades as the Montreal Protocol continues to take effect. In addition, the anthropogenic release of hydrocarbons alters the global environment in ways that we are continuing to discover. For example, our recent measurements have revealed major alkane enhancements in the near-surface atmosphere of the southwestern United States, which we attributed to emissions from the extensive U.S. oil and natural gas reserves [*Katzenstein et al.*, 2003]. These results suggest that inventory estimates of total U.S. natural gas emissions of methane and other light alkanes might be underestimated, and show that emissions from the oil industry have yet another, previously unknown effect on the atmosphere.

Table 1. Partial list of target gases commonly available from whole air sample collection. Other species can be added for specific tracer studies, or for qualitative identifications from composition investigations, e.g., full scan mass spectra.

Ethane	2-Methylpentane	DMS	CCl ₃ F (CFC-11)
Ethene	3-Methylpentane	OCS	CCl ₂ F ₂ (CFC-12)
Ethyne	Benzene	Methyl Nitrate	CCl ₂ FCClF ₂ (CFC-113)
Propane	Toluene	Ethyl Nitrate	CClF ₂ CClF ₂ (CFC-114)
Propene	<i>o</i> -Ethyltoluene	<i>n</i> -Propyl Nitrate	CH ₃ Cl
<i>n</i> -Butane	<i>p</i> -Ethyltoluene	<i>i</i> -Propyl Nitrate	CH ₂ Cl ₂
<i>i</i> -Butane	<i>m</i> -Ethyltoluene	2-Butyl Nitrate	CHCl ₃
1-Butene	1,2,4-Trimethylbenzene	2-Pentyl Nitrate	CCl ₄
cis-2-Butene	1,3,5-Trimethylbenzene	3-Pentyl Nitrate	CH ₃ CCl ₃
trans-2-Butene	<i>o</i> -Xylene	Nitrous Oxide*	CHCl=CCl ₂
Isobutylene	<i>m</i> -Xylene	SF ₆	CCl ₂ =CCl ₂
1,3-Butadiene	<i>p</i> -Xylene	Methane*	CH ₃ Br
<i>n</i> -Pentane	Ethylbenzene	CO	CH ₂ Br ₂
<i>i</i> -Pentane	δ-Limonene	HFC-134a	CHBr ₃
Isoprene	α-Pinene	HCFC-141b	CH ₃ I
<i>n</i> -Hexane	β-Pinene	HCFC-142b	CHClF ₂ (HCFC-22)
		*and isotopes	CBrClF ₂ (H-1211)

Even as faster sensors are developed, the UC-Irvine whole air sampler will remain a unique resource for the community. The whole air sampler addresses a community need with a new approach made possible by advances in laboratory trace gas detection. Gases that are of long-term interest and would be targeted during the SOFIA project include compounds related to stratospheric ozone depletion (e.g. CFC-11, CFC-12, CFC-113, CH₃CCl₃, CCl₄, CH₃Br), gases that affect tropospheric O₃ formation and the oxidative capacity of the atmosphere (e.g. ethane, propane, *n*-butane), and gases that play important roles in the formation of cloud condensation nuclei (e.g. DMS). Other gases can also be targeted according to planned science objectives.

THE ADVANCED WHOLE AIR SAMPLER



Fig. 1. Automated whole air sampler flown on the NASA WB-57 during the PreAVE mission in January 2004. This sampler incorporated a 4-stage bellows pump, 50 1.5-L canisters and a control electronics box (not shown), and weighed approximately 270 lbs.

Design Features.

The whole air sampler is composed of self-contained sampler modules (25 canisters each) that incorporate all the necessary pneumatic control valves and operational components for autonomous sample collection. This design allows for routine use in the field without the requirement of a dedicated on-board operator. A summary of the instrument is given in Table 2. The sample modules incorporate either 1 L or 400 mL canisters for sample collection. The canisters are pressurized with a high purity bellows pump to approximately 3 atmospheres, providing 3.0 or 1.2 std L for analysis, depending on the cylinder size. Pneumatically-controlled bellows valves provide high-purity, automated cylinder closure. The sampler design is able to incorporate either a 2-stage or 4-stage pumping capability, depending on sample requirements. Pump speed is a function of ambient pressure, and estimates from our current system indicate that a 4-stage system could pressurize the larger 1 L canisters in about 1 minute in the lower stratosphere.

Table 2. Summary of Whole Air Sampler for SOFIA

General	
<i>Location in aircraft:</i>	Standard rack mounting
<i>Size (estimated):</i>	17" wide × 44" tall × 16" deep
<i>Weight (estimated):</i>	<200 lbs
<i>Power (estimated):</i>	One 2-stage pump, 115 V/400 Hz, 3-phase, 600 W max. 28 V DC, <100 W
<i>Sample integration times:</i>	<10 sec – 60 sec depending on altitude and configuration
<i>Sample control:</i>	PC104 stack, or equivalent Programmable sample pressure, sample frequency On-demand sample override
Components	
<i>Sample module:</i>	25 samples per module, 2 modules per flight
<i>Canisters:</i>	1 L, stainless steel (passivated) (250 total) 0.4 L, stainless steel (passivated) (250 total)
<i>Canister valve:</i>	Parker mini-pneumatic bellows valve, stainless steel
<i>Sample manifold:</i>	1/2" stainless steel, welded with VCR connectors
<i>Sample compressor:</i>	Senior Flexonics, Lightweight flight-ready air compressor Wetted surfaces 300 series stainless steel (except for Teflon gasket in valve assembly)
<i>Pressure relief:</i>	TAVCO Absolute Pressure Regulator
<i>Pressure transducer:</i>	Ultra High Purity, SETRA #216, 0.1–5.1 V DC
Advantages	
	Proven technology/approach
	Wide use/application in atmospheric science
	Simple inlet
	Advanced analytical application
	Capability for isotope measurement

An advantage of the whole air sampler is the relatively simple inlet requirement. A simple unheated probe has been used successfully in the past. An inlet location for example on the top, aft aperture plate would be ideal. Location on the top, aft aperture plate should not require de-icing capability.

Sample Collection.

The sample collection control system is based on a PC104 computer and solid state relay operation. This system has operated well in all environments, from high altitude balloon sampler control, to automated control in ER-2 and WB-57 installations, to P-3B and other tropospheric aircraft installations. The system offers flexible control for on-board “collection on demand” sampling as well as pre-programmed sample intervals. The system also allows for conditional sampling based on external parameters (e.g. particle plumes, pressure, other trace gas concentrations, etc.).

During SOFIA, the sampling frequency will be determined based on the specified scientific objectives of any given flight. We anticipate that the majority of our sampling will occur during ascents and descents in the troposphere, with a few samples (e.g. one per hour) collected in the stratosphere. During ascents and descents, our objective is as tight a sampling resolution as possible, bearing in mind the finite number of canisters that are available on each flight. Because our canisters fill more slowly at lower atmospheric pressures, sampling would occur at a lower resolution during the aircraft’s ascent (when it is heavy with fuel and has a slow ascent rate), and at a higher resolution during the aircraft’s descent (when the aircraft is lighter and can achieve faster descent rates). For example, a routine, automated sampling strategy once the aircraft reaches the stratosphere could be one sample per hour in the stratosphere, a sample every 15 minutes during the hour prior to the aircraft’s descent, continuous sampling in the tropopause region and down to 25,000 ft, and a sample every 2,000 ft until landing. During the aircraft’s descent, the sampling resolution depends on the descent rate and the external atmospheric pressure. For example, a fill-time of 1-minute and a descent rate of 1,000 ft/min would yield a sample integrated over 1,000 ft, whereas a faster 30-second sample (under higher atmospheric pressure) at the same descent rate would give a 500 ft integrated sample. Our specific sampling strategy will be determined at a later date, once the typical aircraft ascent and descent rates are known, and in accordance with the planned science objectives.

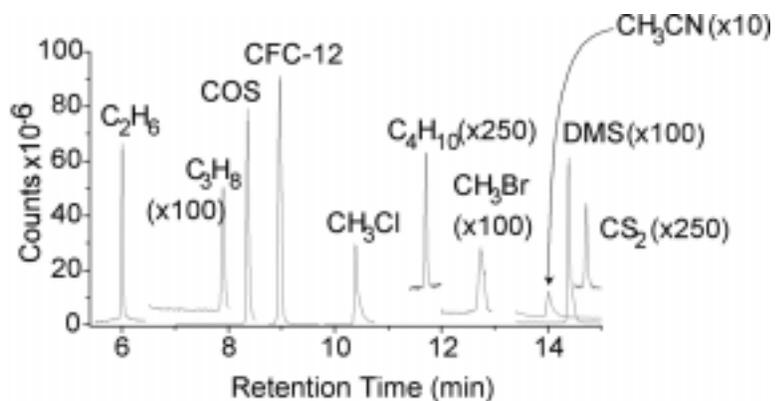


Fig. 2. Selected ion chromatograms from analysis of selected trace gases in 48 cc STP of Cape Grim air (CMDL flask #0064, collected 12/23/03) using the UCI Autospec mass spectrometer.

TRACE GAS ANALYSIS

New technology allows trace gas analysis to be performed on small samples (<100 mL), which leaves sufficient sample in each canister for replicate analysis, for analysis with other instrumentation, or for isotopic studies. By comparison, larger volume sample cylinders add little weight, are compatible with more conventional analytical techniques now in routine use, and may be used for isotopic studies. A combination of canister sizes or other specialized canisters can be incorporated into each module as required by planned scientific goals and flight profiles.

Micro-sample analysis.

An important technological advance that allows mini-canister collection in the SOFIA whole air sampler is the application of high sensitivity mass spectrometric instruments to atmospheric samples. The analysis is based on detection using a Micromass Autospec Ultima mass spectrometer configured with an HP-5890 Gas Chromatograph and a DB5 capillary column. The inlet system is constructed from stainless steel tubing and bellows valves and was constructed specifically for the analysis of small air samples. During routine analysis, a 50 cc sample is drawn through a 1/8” glass-bead filled cryotrap immersed in

liquid nitrogen, and the volume of air in the sample is determined barometrically in a calibrated volume. A small aliquot of pptv-level gas standard (20 cc) containing ^{13}C -labelled isotopomers of the analytes of interest is added to the sample to provide an internal reference for quantification. The sample is transferred to a small bore focusing loop using He carrier gas, then thermally injected onto the GC column, which is thermally programmed to ramp from -50 to 100°C . With the use of isotopically-labelled internal standards, the precision of the analysis is better than 1%.

Even for non-halogenated hydrocarbons, such instruments have considerably higher sensitivity than conventional quadrupole mass spectrometers by virtue of the much higher acceleration potentials imposed on the ions during analysis, improved optics, and more sensitive detection electronics. Above is an example of a whole air analysis illustrating the capability of the UC-Irvine Autospec instrument (Figure 2). The analysis shown includes a range of compounds including hydrocarbons, a chlorofluorocarbon (CFC-12), organohalogens (CH_3Cl and CH_3Br), sulfur compounds (COS , CS_2 , and DMS), and acetonitrile (CH_3CN). These results demonstrate the remarkable sensitivity of the instrument and its suitability for the detection of a wide range of relevant trace gases during the SOFIA mission.

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