## Whole Air Sampler

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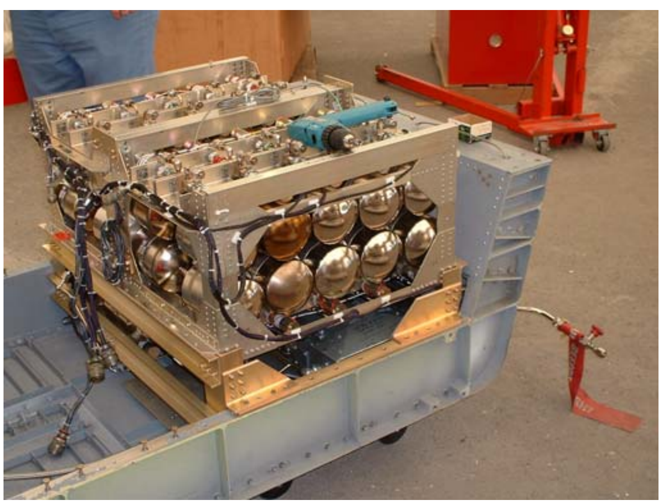
The trace gases that we have routinely measured from whole air samples in tropospheric and stratospheric platforms are listed in Table 1. The list of compounds includes trace gases with sources from industrial midlatitude emissions, from biomass burning, and from the marine boundary layer, with certain compounds (e.g. organic nitrates) that have a unique source in the equatorial surface ocean. The use of a broad suite of tracers with different sources and lifetimes provides powerful diagnostic information on air mass history and chemical processing that currently is only available from measurements from whole air samples. Previous deployments of the whole air sampler have shown that the sampling and analytical procedures employed by our group are capable of accessing the wide range of mixing ratios at sufficient precision to be used for tracer studies. Thus, routine measurement of species, such as methyl iodide, at $<= 0.1 \times 10^{-12}$ mole fraction, or NMHC at levels of a few x $10^{-12}$ mole fraction are possible.

In addition to the tracer and validation aspects of the whole air sampler measurements, we measure a full suite of halocarbon species that provide information on the role of short-lived halocarbons in the tropical UT/LS region, on halogen budgets in the UT/LS region, and on continuing increasing temporal trends of HFCs (such as 134a), HCFCs (such as HCFC 141b), PFCs (such as $C_2F_6$), as well as declining levels of some of the major CFCs and halogenated solvents. The measurement of those species that are changing rapidly in the troposphere also give direct indications of the age and origin of air entering the stratosphere across the tropical tropopause. Thus, several estimates of air transport rates and age will be available from the measurement of species proposed here, plus the measurement of $CO_2$ and $SF_6$ by others on the WB-57.



***Physical Description and operation of the WAS.*** The UM sampler (formerly NCAR) has flown in an automated version a number of airborne platforms. In the automated configuration, metal valves on the sample canisters are turned with external motors. Open and close commands are sent from a small processor that is programmed with sample pressure, time, and frequency information. In Figure 1, we show the recent version flown on the NASA WB-5 7 during the AVE missions. This sampler incorporated a 4 stage bellows pump, 50 1.5 liter canisters, and a control electronics box (not shown here) and weighed approximately 270 lbs.

**Table 1.** Selected compounds analyzed in WAS samples, approximate atmospheric lifetimes (yrs), and predominant source (N=natural; A=anthropogenic).

| | Yrs | Source | | Yrs | Source |
|---|---|---|---|---|---|
| **Chlorofluorocarbons** | | | **Organic Nitrates** | | |
| CFC-11 ($CCl_3F$) | 50 | A | Methyl nitrate($CH_3ONO_2$) | 0.08 | A/N |
| CFC-12 ($CCl_2F_2$) | 102 | A | Ethyl nitrate($C_2H_5ONO_2$) | 0.04 | A/N |
| CFC-113 ($CCl_2FCClF_2$) | 85 | A | Propyl nitrates($C_3H_7ONO_2$) | 0.03 | A/N |
| CFC-114 ($CClF_2CClF_2$) | 300 | A | Butyl nitrates ($C_4H_9ONO_2$) | 0.02 | A |
| CFC-115 ($CF_2ClCF_3$) | 1700 | A | Pentyl nitrates ($C_5H_{11}ONO_2$) | 0.02 | A |
| **Halons** | | | **Non-Methane Hydrocarbons** | | |
| CFC-12b1 (Halon 1211,$CF_2ClBr$) | 20 | A | Ethane ($C_2H_6$) | 0.2 | A |
| CFC-13b1 (Halon 1301, $CF_3Br$) | 65 | A | Ethyne ($C_2H_4$) | 0.06 | A |
| CFC-114b2 (Halon 2402, $C_2F_4Br_2$) | 20 | A | Propane($C_3H_8$) | 0.04 | A |
| **Hydrochlorofluorocarbons/ Hydrofluorocarbons** | | | Isobutane($C_4H_{10}$) | 0.02 | A |
| HCFC-22 ($CHF_2Cl$) | 13 | A | n-Butane ($C_4H_{10}$) | 0.02 | A |
| HCFC-141b ($CH_3CFCl_2$) | 9.4 | A | Isopentane ($C_5H_{12}$) | 0.01 | A |
| HCFC-142b ($CH_3CF_2Cl$) | 19.5 | A | n-Pentane ($C_5H_{12}$) | 0.01 | A |
| HFC-134a ($C_2H_2F_4$) | 14 | A | Isoprene ($C_5H_{10}$) | hrs | N |
| **Solvents** | | | Benzene ($C_6H_6$) | 0.04 | A |
| Carbon Tetrachloride ($CCl_4$) | 40 | A | Toluene ($C_7H_8$) | 0.01 | A |
| Methyl Chloroform($CH_3CCl_3$) | 4.8 | A | C2-Benzenes ($C_8H_{10}$) | <.01 | A |
| Tetrachloroethylene ($C_2Cl_4$) | 0.3 | A | a-Pinene ($C_{10}H_{20}$) | hrs | N |
| Methylene Chloride ($CH_2Cl_2$) | 0.3 | A | **Other** | | |
| Chloroform ($CHCl_3$) | 0.4 | A | Methane ($CH_4$) | 9 | A/N |
| Trichloroethylene($C_2HCl_3$) | 0.02 | A | Carbon Monoxide (CO) | 0.4 | A/N |
| **Methyl Halides and related** | | | Nitrous Oxide ($N_2O$) | 115 | N |
| Methyl Bromide($CH_3Br$) | 0.8 | A/N | Carbonyl Sulfide (COS) | 30 | N/A |
| Methyl Chloride ($CH_3Cl$) | 1.5 | N | Dimethyl Sulfide ($C_2H_6S$) | <.01 | N |
| Methyl Iodide ($CH_3I$) | 0.01 | N | | | |
| Methylene Bromide($CH_2Br_2$) | 0.4 | N | | | |
| CHxBryClz | 0.1 | N | | | |
| Bromoform ($CHBr_3$) | 0.1 | N | | | |