

# Rationale and Methods for Archival Sampling and Analysis of Atmospheric Trace Chemical Contaminants On Board *Mir* and Recommendations for the *International Space Station*

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## FOREWORD

This document was prepared as a result of the collaborative efforts of toxicology, engineering, and analytical chemistry experts in the United States (U.S.) and Russia who are intimately involved with current spacecraft atmospheric monitoring and contamination control and the development of the *International Space Station (ISS)*. It is a synopsis of the joint work of the Environments Subgroup of Medical Working Group 8 and was prepared by the Subgroup participants representing the United States and NASA. This document has been reviewed and accepted by the Russian participants of the Subgroup, namely:

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## TECHNICAL MEMORANDUM

# RATIONALE AND METHODS FOR ARCHIVAL SAMPLING AND ANALYSIS OF ATMOSPHERIC TRACE CHEMICAL CONTAMINANTS ON BOARD *MIR* AND RECOMMENDATIONS FOR THE *INTERNATIONAL SPACE STATION*

## 1.0 INTRODUCTION

The *Mir* space station trace contaminant data provided to NASA by Russian scientists in April 1994 for *Mir* missions 10 through 13 indicated that selected contaminants at times exceeded U.S. and Russian long-term exposure limits. The benzene data from these missions were of particular concern due to an apparent off-nominal event that occurred during *Mir* 10. Benzene concentrations during this mission varied over a range of 5 orders of magnitude. Concentrations were observed most frequently in the 1–10 mg/m<sup>3</sup> range. The NASA Spacecraft Maximum Allowable Concentration (SMAC) for benzene is 0.2 mg/m<sup>3</sup>, which is 10 times lower than the Russian limit of 2 mg/m<sup>3</sup>. Since the first U.S. astronaut was scheduled to fly on board *Mir* 18, three groups began to assess trace chemical contaminant concentrations during *Mir* 17. More detailed information concerning the air quality sampling conducted during *Mir* mission 17 is found in references 1–4. Since *Mir* 17, additional samples have been collected during *Mir* 18 and 19. Results from these missions are still under analysis.

Three different organizations collected cabin air samples during *Mir* 17. These organizations were the NASA/Johnson Space Center (JSC) Toxicology Laboratory, the Boeing Analytical Services Laboratory, and the Russian State Scientific Center Institute of Medico-Biological Problems (IMBP). As part of the shuttle/*Mir* program, NASA/JSC provided a Solid Sorbent Air Sampler (SSAS) for collecting time-integrated air samples. The SSAS has been used by NASA since the mid-1980's to collect samples of cabin air from the space shuttle and Spacelab. Boeing's established contract with Rocket Space Corp. (RSC) Energia for flight experiments provided a second avenue by which NASA could assess trace contaminants in *Mir* cabin air. This program was managed by NASA/Marshall Space Flight Center (MSFC) for NASA Headquarters Office of Life and Microgravity Sciences and Applications (Code U). Boeing provided stainless steel canisters for collecting grab samples. The SSAS and Boeing canisters were delivered to the *Mir* space station on February 15, 1995, via the Progress 226 resupply vehicle. From the Russian side, the IMBP routinely collects and analyzes air samples during each *Mir* mission. The IMBP provided sorbent tubes for collecting grab samples of *Mir* cabin air. All the samples were returned in the Soyuz spacecraft at the conclusion of *Mir* 17.

In order to better understand the results from analysis of the air samples collected on board *Mir*, it is necessary to have a detailed understanding of the sample collection and analysis methods used by the three laboratories. The following discussion provides rationale for sampling and brief descriptions of the methods used by each laboratory, examines the comparability of the data obtained from the different laboratories, and presents rationale and recommendations for methods to be used during future studies on board the *Mir* space station and the planned *International Space Station (ISS)*.

## 2.0 RATIONALE AND OBJECTIVES FOR SAMPLING

The primary reason for collecting and analyzing cabin air samples on board *Mir*, the *ISS*, and other spacecraft is to assess cabin air quality for crew health purposes. Both toxicology and engineering disciplines work together toward this common end. Toxicology is concerned with limiting the risk to crew health from chemical sources, setting exposure limits, and analyzing air samples to determine how well these limits are being met. Engineering provides the means for minimizing the contribution of the various contaminant generating sources by providing active contamination control. The following toxicological and engineering considerations must be addressed by any cabin air sampling program.

### 2.1 Toxicological Rationale

There are many normal and accidental sources of air contamination that can pollute spacecraft cabin air. In this complex environment, there is a moderate risk that the crew will be exposed to pollutants that affect their health and performance. To assess the health threat from accumulation of pollutants, periodic air samples must be taken in areas most often occupied by the crew. Spatial and temporal variations must be addressed by the sampling protocol and limitations to each method must be considered. Toxicological considerations have a direct bearing on the type of analytical methods that should be applied to the samples. Analytical factors that must be considered are the following:

- Sensitivity
- Specificity
- Accuracy
- “Blind spots.”

Because of the toxicological methods used by the United States (U.S.) to assess the air quality of mixtures of pollutants, the analytical method should be sensitive to concentrations below one-tenth the SMAC for each contaminant. The method should have >95-percent certainty in the specific identification of each compound and the accuracy of the concentration measurement should be  $\pm 33$  percent of the true concentration. Finally, the analytical method should minimize “blind spots” by limiting the number of important compounds that cannot be identified. Gas chromatographic (GC) methods coupled with mass spectrometry (MS) methods have achieved the toxicological goals outlined above.

### 2.2 Engineering Rationale

Cabin air quality is a direct result of the design and operation of the various onboard systems of a spacecraft, particularly the Environmental Control and Life Support System (ECLSS). As shown in figure 1, a spacecraft cabin atmosphere is quite complex, with many external and internal factors acting upon it. Only by deploying well-designed contamination control systems and selecting carefully screened materials can acceptable air quality be maintained. Even with this careful attention given to contamination control during the design process, the buildup of trace chemical contaminants from spacecraft hardware, crew metabolic processes, and most routine activities is a persistent concern.

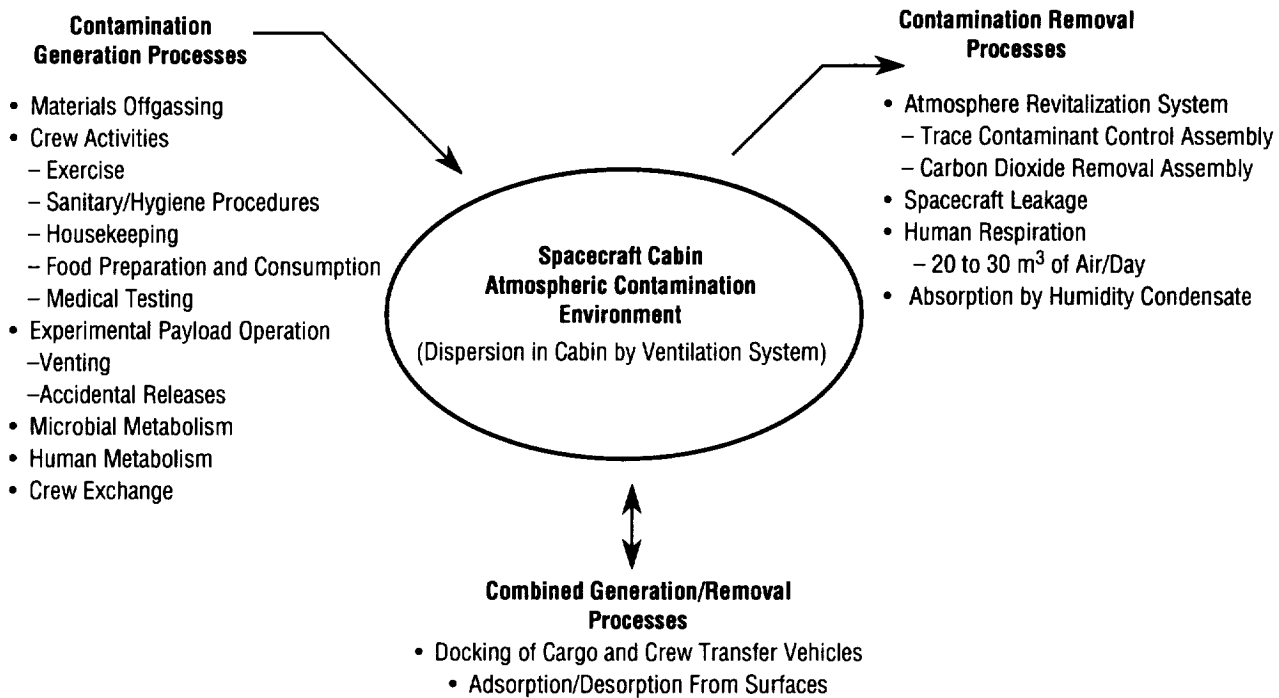


FIGURE 1.—Factors affecting contamination of a spacecraft cabin.

A cabin air sampling program initiated to verify that crew health is not compromised by breathing the cabin air also provides valuable information on the design and operation of the ECLSS. The archival data collected by toxicologists are important to engineers because they provide a statistical basis for designing contamination control systems and defining the magnitude of their design margin. The toxicological requirements for sensitivity, specificity, and accuracy of the overall sampling program help ensure a reliable contamination control system design.

Validation of the spacecraft contamination control system design is also provided by an archival sampling program. Until the contamination control system is actually deployed on board the spacecraft, historical data from the shuttle and Spacelab materials selection, ground-based test data, and on-orbit archival sampling data are used to predict how well the contamination control system performs. This approach has been used successfully for Spacelab missions that used materials offgassing data to predict concentrations. Cabin air sampling archival data were used to refine the generation rates used in these predictions. For the *ISS*, no archival or materials offgassing data are available; therefore, the Spacelab historical data have been used to design the contamination control system and predict its performance.<sup>5</sup> The limitation with this approach is that the Spacelab data are for a short-duration mission. Also, it has been assumed that contaminant generation from Russian spacecraft hardware is similar in magnitude to U.S. hardware. An archival cabin air sampling program on board *Mir* will provide data on the performance of the contamination control system that has been in service for many years and will provide an assessment of the relative magnitude of contaminant generation. The results of such a program provide input to space station contamination control system models to more accurately reflect both the U.S. and Russian spacecraft contamination control system loads.

### **2.3 Objectives**

The primary objectives of the archival cabin air sampling program that address the specific requirements for both disciplines are the following:

- To determine the average background atmospheric contamination environment.
- To understand spacecraft cabin atmospheric trace chemical contaminant concentration dynamics during nominal operations.
- To monitor accidental releases of contaminants.

### 3.0 SAMPLING EQUIPMENT AND METHODS

Air samples were collected from the *Mir* cabin by two proven methods. One involves using evacuated canisters to collect whole air samples and the other involves using sorbent tubes to concentrate contaminants onto a resin-based material. Both of these methods have a long history of use in monitoring air quality in spacecraft and ambient air.<sup>6-9</sup>

Sampling methods used during *Mir* 17 involved manually collecting grab samples using canisters (Boeing) and sorbent tubes (IMBP) and automatically collecting time-integrated sorbent samples using the SSAS (NASA/JSC). All samples were collected near the central control post in the *Mir* base module.

The following discussion describes the sampling techniques used by the different organizations and compares their advantages and limitations. Although NASA/JSC canisters were not used during *Mir* 17, the NASA/JSC canister sampling method will be discussed because of its use during shuttle flights and plans for its use during the Phase 1A (*Mir* 18-19) and Phase 1B (*Mir* 21-24) programs. Similarly, a method for formaldehyde monitoring will also be discussed.

#### 3.1 Description of Canister Sampling Methods

The canisters used by NASA/JSC and Boeing are manufactured and sold by Scientific Instrumentation Specialists (SIS) located in Moscow, ID. As received from SIS, the NASA/JSC and Boeing canisters are identical except for their capacities, which are 300 mL (NASA/JSC) and 500 mL (Boeing). The inside surfaces of the stainless steel canisters are passivated by the Summa™ electropolishing process to provide a more inert surface and thus minimize degradation of organic compounds. The passivated canisters have been studied and used by the U.S. Environmental Protection Agency (EPA) for more than 10 yr. EPA has published Method TO-14 with detailed procedures for using the canisters to collect and analyze ambient air samples for nonpolar organic volatiles.<sup>10</sup> The canisters are configured with a Nupro (Model 4HS) stainless steel bellows valve equipped with a valve torque knob designed to prevent overtightening. The canisters are received from SIS, having been helium leak-tested to 10<sup>-9</sup> standard cc/sec and cleaned to <0.1 ppb of total nonmethane hydrocarbons.

Both Boeing and NASA/JSC laboratories provide additional preflight verification of the canisters for maintaining a vacuum and cleanliness. The canisters are cleaned between each use by at least three evacuation and pressurization cycles using humidified and purified air. Cleanliness is verified by subjecting the canisters to the method of analysis prior to use (proofing). Descriptive schematics and characteristics of the NASA/JSC and Boeing canisters are provided in appendix A. Further descriptions of the current NASA/JSC canister sampling method and the Boeing method used during *Mir* 17 are presented in the following discussion.

### 3.1.1 NASA/JSC Canister Method

Preflight preparation of the canisters requires a series of steps that must meet requirements specified in the NASA/JSC Toxicology Laboratory standard operating procedures and NASA/JSC Safety, Reliability, and Quality Assurance (SR&QA) documents. These steps include the following:

- Test Preparation Sheets (TPS) are written to control handling of the hardware according to NASA SR&QA requirements during the preflight preparation for a mission.
- The TPS is taken to Bonded Stores where the flight canisters are released to the Toxicology Laboratory for preflight preparation.
- High-vacuum leak checks are performed on flight and ground-control canisters.
- The canisters are thoroughly cleaned and proofed to 5 ppb per compound by GC/MS analyses followed by evacuation to  $10^{-5}$  torr.
- Surrogate standards are added to flight and ground-control canisters (*Mir 21* and subsequent flights).
- Flight canisters are labeled and tagged according to the NASA-released drawings, inspected by SR&QA, and returned to Bonded Stores.
- A final approval for shipment is obtained from SR&QA.

Surrogate standards (*Mir 21* and subsequent flights) are added to canisters before they are delivered for missions. These standards are dosed into the canisters as humidified (50 percent relative humidity) gas mixtures. Internal standards are introduced along with the sample during the analytical procedures postflight. This approach improves the ability to detect and differentiate bias effects that might occur during the transport, storage, and return of the samples for analysis and those that might occur in the analytical system. The surrogate standards were selected to represent compounds with a broad range of volatilities and polarities. This broad range is important because compound recoveries depend on their volatility and polarity.

As part of the validation process for a broad-based surrogate standard, the possibility was considered that surrogate standards might be lost during the actual collection of the cabin air sample. Since placing a check valve upstream of the canister valve was considered risky because of potential losses on surfaces that are not Summa™-passivated, a short study was conducted to determine the degree of surrogate loss during the relatively fast pressure equilibration process that occurs during sample collection. Results indicated no significant loss (<5 percent) of surrogate compounds when compared to surrogate standards remaining after a relatively slow pressure equilibration process. Consequently, a check valve was considered unnecessary.

Water is not added to the NASA/JSC canisters beyond what is present in the sampled air. Experience has shown that it is unnecessary for good recovery of nonpolar compounds and may increase the bias effects for some polar compounds. Many of the contaminants observed in spacecraft cabin air are polar or oxygenated compounds.

In addition to the NASA/JSC Toxicology Laboratory quality assurance/quality control (QA/QC) program, the NASA QA/QC program places strict requirements on handling, preparing, and delivering flight hardware for a space mission. Complete documentation for all preflight and postflight handling

and inspection of the hardware is required. This documentation includes NASA-released drawings; hardware certification procedures; and chain-of-custody, Bonded Stores, and shipping/receiving records. In-flight procedures for the use of the hardware are thoroughly reviewed with the crew in several pre-flight training sessions. Additionally, in-flight procedures are provided on the hardware, as well as the in-flight procedures manuals.

### 3.1.2 Boeing Canister Method

After the flight canisters were cleaned and prepared for *Mir* 17, Boeing reserved three canisters that were treated in the same manner as the flight canisters to serve as ground controls. Seven out of the eight Boeing flight canisters were new and had never been used for standards or sample collection. One used canister was substituted for a flight canister that failed during flight certification testing.

Boeing validated modifications to the canister method for assessing the *Mir* ambient air for two reasons. First, payload constraints required the shipment of small 0.5-L canisters. The implementation of 0.5-L canisters with subambient pressure sampling required direct injection of water standards to assure collection of an adequate sample volume to achieve detection limits needed for evaluating the data. Second, the concern regarding benzene resulted in an experimental design that placed enhanced emphasis on the measurement of that parameter. Enhancement of the method for benzene involved the incorporation of  $d_6$ -benzene in the canisters before flight. Simultaneous addition of both surrogates and internal standards provides the following benefits:

- Under certain conditions, adding additional water to the canister provides enhanced canister surface inertness.
- Adding the same amount of excess water to both sample and calibration standard canisters normalizes and reduces bias effects for measurement of polar water soluble organics.
- Adding both surrogates and internal standards simultaneously from a common solution improves the accuracy and precision of surrogate recovery to instrumental accuracy and precision rather than overall method accuracy and precision. This improves the capability to detect bias effects that might occur during the time of transport, storage, and return of the samples for analysis.

The fundamental changes described above required the addition of a one-way check valve to the sampling canister to prevent or minimize the loss of the surrogates and internal standards during sampling. The check valve was designed to equilibrate at 1 psi below the ambient pressure of the sampling environment, and provided a relatively slow stepwise pressure equilibration sampling process which prevents or minimizes the loss of the surrogates and internal standards that could have occurred from a ballistic equilibration process with possible back diffusion and “rebound” effects.

Boeing developed sampling plans that provided general sampling instructions and specific procedures detailing the canister’s use. The procedures defined the hardware configuration; provisions for documenting sample custody, location, dates, and time; stepwise detailed procedures for proper use of the equipment; and sampling and equipment verification documentation requirements. Sample chain-of-custody was documented on a chain-of-custody form that accompanied the sample canisters. Custody seals were developed for the canister shroud, which protected the canister valve during transport and

storage. Video documentation of the integrity of this seal was obtained upon receipt of equipment on the *Mir*, and breakage of those seals by the cosmonauts was also documented.

The sampling plans were used as a training document to develop a training video at the Russian Mission Control Center. The training video summarized descriptive information, procedures, and precautions to the cosmonauts for utilizing the canister for sample collection.

### **3.2 Sorbent Tube Sampling Methods**

The NASA/JSC and IMBP sorbent tube sampling methods use Tenax GC as the trapping medium for volatile organic compounds. Tenax has been used for many years by the EPA for this application. The following discussion provides brief descriptions of the two methods.

#### **3.2.1 NASA/JSC Solid Sorbent Air Sampler**

The NASA/JSC SSAS is designed to collect seven time-integrated samples over specified intervals, typically 24 hr. The SSAS is equipped with a sample pump powered by four C-size alkaline batteries. The SSAS assembly includes eight sorbent tubes (the eighth tube is not used) containing 0.5 g of Tenax connected to the pump through an 18-port rotary valve. The valve is turned manually to select each tube. The SSAS includes an electronic timer module which pulses the pump on and off at regular intervals to provide a pump duty cycle that allows for the collection of approximately 0.5 to 3.0 L of air within a 24-hr period, depending on the application. The timer is preset before flight to provide the desired sampling rate. The SSAS is equipped with an inlet that contains a filtering screen. Descriptive schematics are provided in appendix B. The flight hardware documentation and chain-of-custody requirements for the SSAS are identical to those previously discussed for the canisters.

**3.2.1.1 Preflight.** The flight hardware documentation and chain-of-custody requirements for the SSAS are identical to those discussed previously for the canisters. Preflight procedures used to prepare the SSAS are the following:

- Each SSAS tube is cleaned with ultrapure nitrogen at 250 °C and proofed to 5 ppb using GC/MS. This procedure is identical to the analysis of samples except that 200 standard cubic centimeters (stdcc) are analyzed in the proofing procedure, whereas 100 stdcc are analyzed during sample analysis.
- Each SSAS tube is dosed with surrogate standards to assess the stability and recovery during postflight analysis.
- Fresh batteries are placed in the unit.
- The airflow rate through each tube is measured in triplicate using a small volume of clean, humidified air. The flow rate is also measured after flight in the same manner.
- The SSAS is sealed in a plastic bag, tagged, and delivered to bonded storage until shipment according to NASA QA procedures and protocol.

**3.2.1.2 In-Flight.** The SSAS was designed to provide automated collection of multiple, time-integrated samples. During normal use on the shuttle, the SSAS pump is activated at the beginning of a mission and a crew member periodically switches the valve to the next tube according to the mission



timeline. Near the end of the mission, the SSAS pump is deactivated, the valve is turned to the “park” position, and the SSAS is stowed. Activation/deactivation and valve switch times are recorded on the SSAS label. During *Mir* missions, the SSAS pump must be activated/deactivated manually and the valve returned to the “park” position for each sample (tube) collected. Procedures for the in-flight use of the SSAS are listed stepwise on the hardware label. Crew member interaction is limited to the following:

- Deploy the SSAS at the designated location.
- Select the sorbent tube by turning the valve indicator knob.
- Initiate sampling by turning the pump switch to the “on” position.
- According to the mission timeline, turn the pump switch to the “off” position and return the valve to the “park” position.
- Document the start and end times for sample collection on the SSAS label.

**3.2.1.3 Postflight.** Postflight handling procedures including shipping, transferring custody, use of Bonded Stores, and documentation requirements are identical to those discussed in the NASA/JSC canister method.

### **3.2.2 IMBP Solid Sorbent Sampler**

The IMBP sorbent sampling method is designed to collect grab samples manually with a hand bellows pump connected to a sorbent tube filled with Tenax GC. The sorbent tube is made of stainless steel and is 150-mm long with a polished inner surface of 5-mm inside diameter. The sorbent tube is threaded at both ends and sealed with threaded end caps containing a Teflon™ seal. Nylon line is used as a lanyard to attach the sealing end caps to the tube to prevent loss in microgravity. A descriptive schematic is presented in appendix C.

**3.2.2.1 Preflight.** The sorbent tubes and materials used to secure the sorbent bed are solvent-rinsed and heat-treated to 300 °C before packing the sorbent. After cleaning, the tubes are packed with an estimated 1 g of Tenax GC using a combination of glass wool and Teflon™ delimiters to secure the bed. After packing, the complete sorbent tube assemblies are conditioned in an oven at approximately 300 °C while passing a stream of inert gas through the tube. After conditioning, the sorbent tube is subjected to analysis to verify cleanliness. The verified clean tubes are hermetically sealed and sent to the *Mir* space station. They are certified for use for a period of 1.5 yr after shipment.

**3.2.2.2 In-Flight.** Air samples are collected through the sorbent tube with a hand-operated bellows pump designated as a model AM-5. The pump is designed to collect 100 cc of air for each complete compression of the bellows. The bellows pump consists of a rubber bellows interfaced to upper and lower plastic mounting plates connected by small metal chains. One of the chains is equipped with an adjustable screw and lock nut to adjust for a calibrated volume of sample pulled by the pump. One of the mounting plates contains a check valve where the bellows air is expelled during compression. The hand pump is equipped with a rubber nipple for attachment of the sorbent tube. The IMBP method specifies that 500 cc of air be collected by five complete compressions of the pump. The instructions specify that both hands be used to compress the pump to ensure accurate volumes are collected. Reference 11 contains more details on the IMBP sampling method.

### 3.3 Formaldehyde Monitoring Method

Formaldehyde concentrations in the shuttle and *Mir* atmospheres have been monitored using a dosimeter badge concept. This method employs a passive diffusion-type monitor consisting of a disposable badge containing a dry sodium bisulfite collector. Formaldehyde reacts with the bisulfite to form a stable compound, sodium formaldehyde bisulfite. In the laboratory, formaldehyde is regenerated from the sodium formaldehyde bisulfite and reacted with chromotropic acid to form a visible purple chromophore. The absorbance of the solution at 580 nm is determined using a spectrophotometer. This formaldehyde measurement method has recently been compared to three diverse analytical methods and was found to provide quite reliable results.<sup>12</sup> Reference 13 provides additional detail on the formaldehyde monitoring method, preflight preparation, in-flight deployment, and postflight analysis. A schematic of the formaldehyde sampler is shown in appendix D.

#### 3.3.1 Preflight

Before flight, the effective uptake rate of the formaldehyde monitors is determined independently and compared to the rate supplied by the manufacturer with each batch of monitors. Monitors are selected from a single batch for each flight to ensure uniformity. Monitors are purchased 3 to 4 mo before flight. The manufacturer states a shelf life of 1 yr. No less than three monitors from each batch are tested for uptake rate from each batch. Average uptake rates cannot deviate by >15 percent from the manufacturer's supplied rate.

The formaldehyde monitoring kit contains monitors that will be exposed during the flight, one to two positive controls, and one to two negative controls. The negative controls remain unexposed and are considered to be trip blanks. The positive controls are exposed in the laboratory to a known quantity of formaldehyde before the flight. Stability of the collected formaldehyde from the time of collection to analysis is provided by the positive controls.

#### 3.3.2 In-Flight

Formaldehyde monitors are deployed in-flight to determine the concentration of formaldehyde in a crew members's breathing zone and in specific areas of the spacecraft. Two types of samples are usually collected—area samples and personal samples. Area sampling involves deploying a sampler in a stationary surface in the spacecraft for at least 24 hr several times during the flight. Personal sampling requires a monitor to be attached to a crew member for at least 12 hr several times during the flight. Crew interaction required is the following:

- Remove formaldehyde monitors from the kit.
- Record mission time and remove cover to start sampling.
- Deploy monitors at designated location.
- After the appropriate amount of time, seal the monitors and record mission time.

#### 3.3.3 Postflight

After the flight, the formaldehyde monitors are returned to the NASA/JSC and analyzed within 2 wk. Postflight handling procedures similar to the canister method are used.

### 3.4 Advantages and Limitations of Sampling Methods

All of the sampling equipment and procedures described above can be used to collect known volumes of air accurately when they are used precisely in a documented and validated manner. Each sampling system has inherent advantages and limitations that are independent of implementation. Some of the factors that must be considered in the use of particular sampling equipment include the following:

- The sampling method must meet the accuracy required for experimental and operational objectives.
- The weight and volume of the flight hardware must be minimized.
- The hardware must be simple and easy to use.
- The hardware must be reliable.
- The costs involved in developing and using the method must be minimized.

With these considerations and knowledge of the features of the different sampling systems, the advantages, limitations, and recommended precautions for the methods applied during *Mir 17* and future spacecraft cabin air sampling efforts can be discussed. The following discussion lists the advantages and limitations of the methods under comparison.

#### 3.4.1 NASA/JSC and Boeing Grab Canister Sampling

The advantages of the canister grab-sampling method include the following:

- The device is easy to operate by opening and closing a valve.
- The canister can be analyzed for trace contaminants multiple times at different dilutions. (The broad range of concentrations of various contaminants found during *Mir 17* were analyzed at different dilutions.)
- The canister has been demonstrated to be stable to nonpolar organic contaminants for extended periods (1.5 yr tested with good accuracy) and at temperatures as low as  $-90\text{ }^{\circ}\text{C}$ .
- The canister sample can be analyzed for other important volatile constituents such as hydrogen ( $\text{H}_2$ ), carbon monoxide (CO), and  $\text{C}_1\text{--C}_4$  hydrocarbons (e.g., methane, ethane), and Freons™ that are not efficiently trapped by Tenax.
- Both canister sampling methods use internal surrogates to improve the reliability of results.

Limitations of the canister grab-sampling method are the following:

- Bias can exist against water soluble organics relative to the Tenax sorbent. Charts illustrating the measured bias for the Boeing canisters can be found in appendix E. A detailed discussion of this limitation can be found in the canister method review by Kelly and Holdren.<sup>14</sup>
- Both canister methods, as currently defined, are limited to grab samples.
- Both types of canisters take up more space per sample than sorbent tubes, thus limiting the use of trip and storage blanks.
- Water can passivate internal surfaces or associate with polar compounds. It is not known exactly how much water is beneficial or deleterious to the recovery of compounds using this sampling method.

Other considerations of the canister grab-sampling method relate to the type of inlet to use. There has been no demonstrated advantage or disadvantage to using a check valve on the canister inlet. A check valve was used on some canisters during *Mir 17* to provide for added sample integrity by preventing loss of the internal surrogate during sampling.<sup>15</sup> However, testing conducted by NASA/JSC has demonstrated that the check valve provides no immediate benefit to the sampling process and that surrogate loss is not a concern.<sup>16</sup> Therefore, the use of a check valve is considered a matter of preference.

### **3.4.2 NASA/JSC Solid Sorbent Sampling Method**

Advantages of the NASA/JSC SSAS are the following:

- The SSAS collects time-integrated samples, typically over a 24-hr period.
- The SSAS collects seven air samples in a compact, rugged, low volume, low mass device.
- Tenax is a good all-purpose sorbent for both polar and nonpolar organic compounds.
- The SSAS can be used to concentrate large volumes of air to improve sensitivity for selected compounds that are well-trapped on the sorbent.
- The SSAS is easy to operate and requires minimal crew member interaction.

Limitations and precautions applying to the NASA/JSC SSAS are the following:

- The 0.5-g bed of Tenax was not designed to provide quantitative retention from a 0.5- to 3.0-L volume for compounds that are poorly retained by Tenax.
- Uncertainties in the airflow through the sorbent tubes can be caused by battery drain or by obstruction of the inlet filter.
- Highly volatile contaminants, such as CO, cannot be trapped with Tenax.

### **3.4.3 IMBP Solid Sorbent Sampling Method**

Advantages of the IMBP solid sorbent grab sampling method are the following:

- The small size and mass of this compact sampling system is appealing with respect to stowage volume and launch mass.
- The system is easy to use and does not require complex procedures.
- The 500 cc sample volume appears to be adequately sized for the Tenax sorbent bed, thus minimizing breakthrough problems; however, experimental validation of breakthrough is required.
- The Tenax sorbent sampling system is good for both polar and nonpolar organic compounds.

Limitations and precautions applying to the IMBP solid sorbent grab-sampling method are the following:

- The accuracy of sample volume collection is dependent on the dedication of the cosmonaut sampler to assure precise use of the equipment. The hand bellows pump must be compressed completely and the number of compressions must be carefully tracked and documented.

- A constant flow rate cannot be maintained with a bellows pump. A controlled flow rate can be critical for trapping some compounds efficiently on certain sorbents. The use of this device with other sorbent trapping systems could require the use of flow restriction devices.
- The rubber nipple used to secure the sorbent tube could wear with age, thus causing inadequate sealing of the sorbent tube to the bellows pump.
- The sampling system is limited to grab sampling.
- The lack of surrogate standards lessens the degree of confidence in the analytical results.
- Highly volatile compounds, such as CO, cannot be trapped with Tenax.

#### **3.4.4 Formaldehyde Sampling Method**

Advantages of the NASA/JSC formaldehyde monitoring method are the following:

- The monitors are small, lightweight, and easy to use.
- The monitors are stable with a shelf life of up to 1 yr.
- Formaldehyde forms a stable product with sodium bisulfite.
- No special resources such as refrigeration are necessary to preserve the sample.

The disadvantage of the NASA/JSC formaldehyde monitoring method is that adequate ventilation must be provided to the face of the monitor.

## 4.0 SUMMARY OF ANALYTICAL METHODS

The following discussion provides summaries of the analysis procedures that were used to analyze samples collected on board *Mir* 17 by the three laboratories or that will be used on subsequent *Mir* and *ISS* flights. Included in the discussion are the NASA/JSC and Boeing canister methods, the NASA/JSC SSAS method, the IMBP sorbent tube method, and the NASA/JSC formaldehyde monitoring method.

### 4.1 NASA/JSC Toxicology Laboratory

#### 4.1.1 NASA/JSC Canister Method

NASA/JSC uses a modification of the basic EPA TO-14 method to analyze grab samples. The modifications were made based upon the size and weight constraints for flight hardware and the nature of contaminants observed in spacecraft cabin air. High levels of carbon dioxide and water vapor are problematic in analyzing spacecraft cabin air and the analytical method addresses these issues. Analytical standards include the basic TO-14 mixture and a lab-prepared standard mixture of polar compounds. The polar components of the mixture were selected on the basis of previous analyses of spacecraft cabin air. Analysis of the canister samples is identical to that of the SSAS after the SSAS tubes are desorbed into canisters. The NASA/JSC method follows the TO-14 method in tuning the mass spectrometer, verifying instrument tune, running system blanks, cleaning and proofing sample canisters, and handling data. The complete volatile organic compound (VOC) analytical method for canister samples is described in reference 17.

The NASA/JSC laboratory uses conventional packed-column gas chromatography for the analysis of gaseous parameters, CO, H<sub>2</sub>, and CH<sub>4</sub>. The complete analytical methods, including QA/QC procedures and acceptance criteria, are summarized in reference 18. The analysis of CO, H<sub>2</sub>, and CH<sub>4</sub> requires three dedicated gas chromatographs equipped with a helium ionization detector, thermal conductivity detector, and flame ionization detector, respectively. The external method of quantification is used. Certified gas standards, in concentrations that bracket sample response, are analyzed with each set of samples to provide a calibration curve.

#### 4.1.2 NASA/JSC Solid Sorbent Sampling Method

The *Mir* 17 SSAS was returned in a sealed bag to the NASA/JSC Building 37 Bonded Stores on April 12, 1995. The hardware was transferred to the Toxicology Laboratory controlled storage cabinet under chain-of-custody control. Details of the analytical protocol are documented by reference 19.

The SSAS sorbent tubes were thermally desorbed under nitrogen flow into cleaned and proofed (verified clean by analysis) Summa™-passivated canisters containing 100 cc of humidified zero-grade air. The canisters were then pressurized with humidified zero-grade air to approximately 14 psia. The final pressure of each canister was measured and the canisters were allowed to equilibrate overnight.

The SSAS pump flow measurements were made in triplicate and compared to preflight measurements in the SSAS Data Worksheet. The difference in preflight versus postflight flows averaged 22 percent from the mean, which exceeds the quality acceptance criterion of  $\pm 15$  percent.<sup>4</sup> As required by the standard operating procedure, the cause of the anomaly was investigated. Past experience from shuttle sampling indicates that deviations greater than  $\pm 5$  percent are rare. The cause of the problem was identified as a “milky-white substance” obstructing the inlet filter screen. Engineering and analytical experts are working together to prevent a future occurrence of this problem. A redesigned inlet filter has been fabricated and tested, and will be used on the SSAS beginning with *Mir 21*.

Before any analysis of samples or standards, the proper tuning, initial calibration, and background levels were verified according to EPA specifications for acceptance criteria. The initial calibration included 68 target compounds, which include 39 TO-14 nonpolar compounds and 29 polar compounds. The polar compounds were selected on the basis of several factors including concentration, frequency of occurrence in previous spacecraft, and inherent toxicity. The GC/MS instrument was initially calibrated for these 68 target analytes in the range of 20 to 400 ppb. Relative response factors, meeting EPA criteria, were determined for each of these. The continuing calibration of the GC/MS was verified daily by analyzing a 100 ppb standard. System blanks were analyzed between all analyses of standards and samples. The desorbates collected in canisters were first analyzed by GC/MS at reduced volume (40 mL) to screen for contaminant concentrations. Following the screen, 100 mL aliquots of the samples were analyzed in duplicate. The averages of the results from the duplicate analyses were reported. Duplicate analyses were in good agreement with each other. Nontarget analytes were quantified by using relative response factors obtained from analytical standards or reference sources. This approach is considered to be superior to assigning an arbitrary relative response factor of 1.

A certified EPA audit sample, containing 18 compounds, was analyzed by the NASA/JSC Toxicology Laboratory. All results were within guidelines for excellent quantitative results. The average percent deviation for all of the audit sample components was 8.9 percent.

In some cases, the SSAS sampling volume exceeds the retention volume (breakthrough volume) for an identified compound. In such cases, the retention volume is used in place of the calculated sample volume for the quantitation calculation. The SSAS sampling rate is adjustable and is based upon a balance between achieving satisfactory detection limits and limiting the number of compounds that require volume corrections. Data supplied by NASA/JSC summarizing the affected compounds and associated correction factors can be found in appendix F. The data for these compounds are considered semiquantitative.

#### **4.1.3 NASA/JSC Formaldehyde Monitoring Method**

Formaldehyde monitors are analyzed according to a National Institute of Occupational Safety and Health (NIOSH) method that uses liquid extraction and chromotropic acid colorimetric methods. This method is documented by reference 13. Exposed monitors are disassembled in the NASA/JSC laboratory and the collection media are placed in test tubes. Formaldehyde-free water is added to the test tube and allowed to stand for 30 min, with occasional agitation. Chromotropic acid reagent is added to each sample followed by the slow addition of concentrated sulfuric acid. The resultant solution is thoroughly mixed and allowed to cool. During this time, color development occurs. Each sample is then

placed into a centrifuge for 10 to 15 min until a clear supernatant is obtained. The sample is then placed in a spectrophotometer and the absorbance is determined at 580 nm. This absorbance is checked versus a reagent blank. The resulting data are regressed using a least-squares fit to obtain a formaldehyde concentration. The regression correlation coefficient ( $r^2$ ) must be 0.98 or better.

#### 4.2 Boeing Analytical Services Laboratory

The *Mir* sample canisters were received April 4, 1995, and placed in locked storage until arrival of Russian technical representatives to witness the analyses. Before analyzing the samples, the GC/MS instrument was initially calibrated with a newly purchased standard containing the EPA TO-14 nonpolar target compounds. The instrument was calibrated in the range of 40 to 500 ppb concentrations. This range was extended by analyzing a 1,000 ppb standard. The extended range met the acceptance criteria of  $\pm 25$  percent. The initial calibration of the instrument was verified by the analysis of three certified samples obtained from EPA. All of the results obtained by the analysis of the certified EPA sample were within the project goal of  $\pm 25$  percent, with the average of the results of all parameters being  $\pm 10.4$ -percent deviation. The instrument was also calibrated for the EPA safe drinking water parameters and a select group of water soluble polar organics. In total, the instrument was calibrated for 82 organic trace contaminants.

Another GC/MS instrument was configured to conduct analysis of IMBP sorbent tube samples utilizing a Tenax-packed column in a manner similar to that used by IMBP. This instrument was calibrated with method standards utilizing a blank IMBP sorbent tube to standardize the instrument.

Before analysis, the sample canister absolute pressures were recorded and the canisters were pressurized to 15 psig and allowed to equilibrate for 24 hr before analysis. Two-hundred-milliliter aliquots of the pressurized samples were analyzed using the fluorobenzene trip internal standard technique of quantification.

A performance test mix was analyzed to verify instrument operating performance for sensitivity, mass tuning, and response factor stability before analysis of any standards or samples. After meeting acceptance criteria for the performance mix, daily continuing calibration verification was performed, and the instrument relative response factors were updated to reflect the current state of the system. All standards, flight samples, and ground control samples were bracketed with instrument blanks to verify system cleanliness for each analysis. Quantification estimates for nontarget analytes were obtained by the comparison of total ion currents of nontarget parameters to the total ion current of the fluorobenzene internal standard.

All pressurizations and sample aliquots were documented carefully to provide the necessary data to compute the gaseous parameters of CO, H<sub>2</sub>, and CH<sub>4</sub>. This is necessary because these parameters were analyzed by the external standard technique for quantification. Low levels of CO and H<sub>2</sub> were analyzed by GC with discharge ionization detection, and the CH<sub>4</sub> was analyzed by GC with flame ionization detection.

Three IMBP sorbent tube samples were analyzed by Boeing using a GC/MS instrument configured with a thermal desorption oven interfaced to a purge and trap device. Calibration standards were



prepared in pressurized Summa™ canisters, and the GC/MS instrument was calibrated through method standardization whereby 500-mL standards were introduced to the analytical system through a blank sorbent tube. External standard calibration of the instrument was achieved for a number of volatile polar and nonpolar compounds that produced reasonable chromatographic peaks for quantification. A number of target analytes failed to produce acceptable peaks due to poor chromatographic behavior on the Tenax-packed column.

### **4.3 IMBP Analytical Laboratory**

IMBP received three sorbent and two canister samples that were collected at times that were within 15 min of collection of the Boeing canister samples. Due to difficulties with Russian-English translation, it is difficult at the time of this writing to describe precisely how the different samples were analyzed. The following discussion summarizes in general terms the IMBP analysis of the *Mir 17* samples.

IMBP conducted sorbent tube and canister analyses for 16 target analytes utilizing various gas chromatographs configured with different types of packed columns selected for resolving and confirming the different target analytes. The sorbent tubes were thermally desorbed and allowed to flow into an expandable syringe at 200 °C. The sealed syringe was placed into an oven at 60 °C until aliquots were injected into the various gas chromatographs equipped with flame ionization detectors.

In this technique, the instruments are calibrated and verified utilizing both static and dynamic calibration standards. Additional method standards were processed to provide an assessment of accuracy.

IMBP also conducted two types of analyses on the canisters provided by Boeing. Aliquots were taken and subjected to their standard analysis by collecting sample concentrates from the canisters. The concentrates were also analyzed by GC/MS utilizing an LKB 9000 GC/MS equipped with a packed column and jet separator. The GC/MS analyses were performed primarily as a qualitative verification of components detected in the sample analyses. The results from those analyses confirmed the identity of 10 trace contaminants from two composite mass spectra containing characteristic ion clusters. The IMBP report stated that acetaldehyde could not be confirmed by their GC/MS system due to interference of CO<sub>2</sub> at 44 daltons. Characteristic ions of a number of Freons™ were noted, but resolution of the Freons™ was not achieved.

### **4.4 Advantages and Limitations of the Analytical Methods**

The analytical methods used in the NASA/JSC and Boeing laboratories to analyze VOC's, CO, H<sub>2</sub>, and CH<sub>4</sub> are very similar. Both laboratories use EPA Method TO-14 with only minor modifications for VOC analyses. Although IMBP did analyze the *Mir 17* canister samples provided by Boeing, the IMBP does not routinely analyze canister samples. Furthermore, the IMBP method is not designed to be a comprehensive method of analysis for VOC's.

#### 4.4.1 NASA/JSC and Boeing Canister Methods

Advantages of the NASA/JSC and Boeing canister analytical methods include the following:

- Both GC/MS inlet systems effectively manage high levels of CO<sub>2</sub> and water without any apparent interference.
- The EPA Method TO-14 is a well-established method that includes well-defined and comprehensive QA/QC procedures and acceptance criteria.
- Both laboratories incorporate surrogate and internal standards in their analytical procedures as well as target analyte standards for accurate identification and quantification.
- Both laboratories attempt to identify and quantify all significant VOC contaminants in the air samples, not just the target analytes.
- Both laboratories use well-established analytical methods for measuring CO, H<sub>2</sub>, and CH<sub>4</sub>.

Limitations of the NASA/JSC and Boeing canister analytical methods include the following:

- Methanol cannot be quantified by the Boeing method because it includes analysis of standards prepared in methanolic solutions. Methanol is a key contaminant for air quality assessment and the function of the water recovery system.
- The NASA/JSC sample inlet system appears to be less efficient at trapping compounds of highest volatility compared to the Boeing system.

#### 4.4.2 NASA/JSC and IMBP Sorbent Tube Methods

Advantages of the NASA/JSC analytical method versus the IMBP method for analyzing sorbent tube samples include the following:

- The use of high-resolution GC/MS allows for a much more comprehensive analysis of samples than does packed-column GC methods.
- Although the use of multiple GC columns for analyzing samples is an improvement over the use of a single column, this method does not provide the same level of confidence for positively identifying compounds as compared to high-resolution GC/MS.

The use of GC/MS provides more confidence in positively identifying compounds; however, the means for supplying the sample to the instrument can serve as a source of methodological error. NASA/JSC desorbs the sorbent tube into a grab canister before introducing the sample into the GC/MS. In principle, it is possible for losses to occur during this operation; however, studies conducted by NASA/JSC have demonstrated that the contribution to methodological error is negligible and is accounted for by the normal error associated with the complete analytical method.<sup>20</sup>

#### **4.4.3 NASA/JSC Formaldehyde Monitoring Method**

The formaldehyde monitoring method has been subjected to rigorous validation. The manufacturer of the monitors has investigated the effects of environmental factors such as temperature, humidity, air velocity, and orientation to airflow on the formaldehyde uptake rate; the accuracy and precision of the method; and the monitor's shelf life.<sup>21</sup> No positive or negative interferences with volatile organic compounds or other aldehydes have been observed during ground verification tests. The sodium bisulfite does not trap phenol or other contaminants that may interfere with the chromotropic acid analytical procedure.<sup>22</sup> These studies have shown that the monitors are an effective means for determining formaldehyde exposures. Key to the monitor's effective use, however, is the need to maintain adequate airflow to its surface at all times. Care must be taken that they are not placed in stagnant air zones. Badges placed on crew members are intended to provide measurements of the air that they breath, while badges placed on surfaces are intended to monitor the environment itself.

## 5.0 COMPARISON OF ANALYTICAL RESULTS OF *MIR* 17 SAMPLES

Multiple samples were taken by each laboratory during the course of the *Mir* 17 mission as documented by references 1 and 4. On March 13, 1995, an SSAS tube, IMBP sorbent tube, and Boeing canister sample were all collected during the same 24-hr period in the *Mir* core module at the central command post. The SSAS sample was a 24-hr integrated sample and the IMBP and Boeing grab samples were collected within 15 min of each other. A general comparison of the results from *Mir* 17 provided by the three laboratories can be made from these data with the understanding that direct comparison of 24-hr averaged data and grab-sample data is only valid if the *Mir* atmosphere is stable during this period. An attempt is made to explain major differences in findings with respect to knowledge of the sampling and analysis methods.

### 5.1 Findings Common to All Methods

Boeing and IMBP samples were collected as grab samples at approximately the same time and location while the NASA/JSC sample was collected over time. Table 1 and figure 2 summarize the data for 16 target parameters for which all laboratories reported findings. The following general comments can be made from these data:

- The data from all laboratories are comparable, considering that the same general trend is followed regarding relative magnitude of concentrations for the different target compounds.
- The Boeing data usually show lower concentrations than the data from the IMBP and NASA/JSC. This was expected since the focus of the Boeing analytical method was nonpolar compounds.
- The IMBP sorbent data for butyl acetate seems to be an outlier from NASA/JSC and Boeing data and from their analysis of the Boeing canister.
- With the exception of butyl acetate, the ratios of highest to lowest concentrations of numbers for compounds detected by all laboratories generally ranged from 1 to 4.
- With the exception of butyl acetate, data from IMBP-analyzed canisters and AK-1 sorbent tubes are good.

NASA/JSC and Boeing analyzed the samples for an expanded number of target compounds and reported tentatively identified compounds. General comments on these data are the following:

- A ratio of 2 or less (0.5–2.0) was exhibited by 11 of 18 compounds.
- With the exception of the chlorofluorocarbons, SSAS data corrected for retention volume are comparable to IMBP sorbent data for polar analytes and to Boeing data for applicable nonpolar compounds.
- Significant differences in nontarget compounds could be attributed to differences in the methods employed in estimating concentrations.
- Considering expected differences in grab and time integrated samples, comparability of the data is good.

TABLE 1.—Data for samples collected on March 13, 1995.

Contaminant	NASA/JSC SSAS	IMBP Canister	IMBP Sorbent Tube	Boeing Canister
Heptane	0.000	0.000	0.000	0.027
Benzene	0.010	0.000	0.000	0.007
Butyl Acetate	0.020	0.040	0.230	0.006
Hexane	0.030	0.000	0.000	0.017
Isopropyl Benzene (C3 Sub)	0.030	0.100	0.100	0.030
Methylethylketone	0.050	0.000	0.000	0.010
Isopropanol	0.060	0.055	0.085	0.034
Acetaldehyde	0.090	0.000	0.160	0.050
Ethyl Acetate	0.140	0.000	0.000	0.029
o-Xylene	0.200	0.100	0.060	0.121
Butanol	0.210	0.200	0.250	0.056
Methanol	0.210	0.100	0.140	NQ
m,p-Xylenes	0.280	0.110	0.090	0.084
Toluene	0.450	0.310	0.260	0.240
Acetone	0.490	0.350	0.400	0.160
Ethanol	1.700	2.800	3.320	1.210

NOTE: Analytes reported as not detected are reported as zero in the table for graphing purposes.

NQ = Not quantified

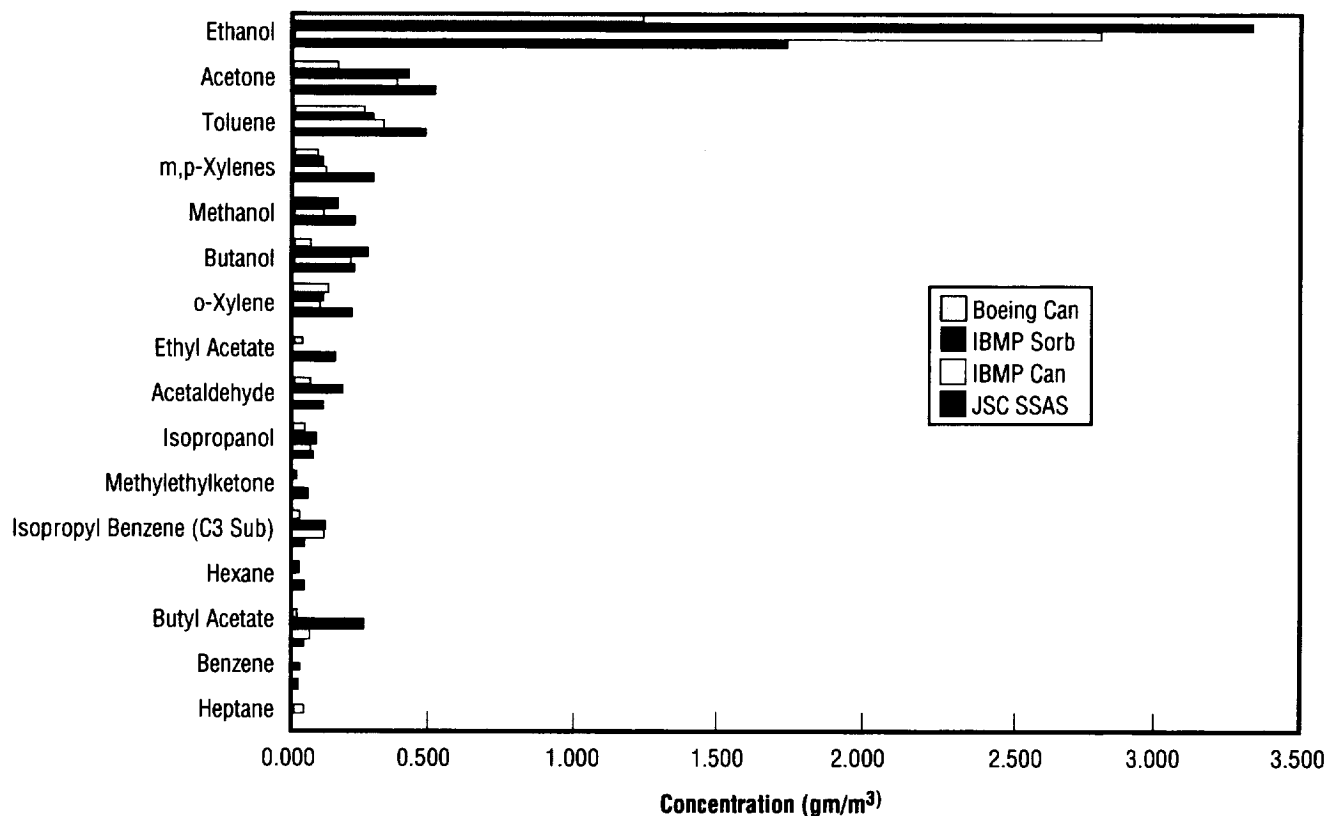


FIGURE 2.—Findings common to all methods.

## 5.2 Discrepancies in Results

Comments summarizing observed discrepancies in results are the following:

- Differences in time-integrated sampling versus grab sampling are to be expected.
- Boeing data showed a negative bias for water-soluble compounds due to the addition of excess water in the canisters.
- Large differences in chlorofluorocarbon results between NASA/JSC and Boeing could be due to their extreme volatility, analytical system precision, differences in quantitative methods for nontarget chlorofluorocarbons, or the retention volume corrections on the SSAS data.
- Boeing detected perfluoropropane and perfluorodimethylcyclohexane at relatively high concentrations compared to NASA/JSC, possibly because of differences in the trapping efficiencies in the Boeing versus NASA/JSC GC/MS inlet systems and/or poor collection efficiencies for these compounds on the SSAS.
- Significant differences in results for target versus nontarget compounds at low concentrations are expected. Discrepancies at low concentrations can be explained by differences in resolution of compounds resulting from different ground-based techniques.
- Significant differences in NASA/JSC versus Boeing data were found for 1-chloro-2-fluoroethane. Boeing searched chromatograms for the presence of this compound and could not find any traces of ions expected for it. This compound could have been masked by high concentrations of other Freons™.
- Significant differences in NASA/JSC versus Boeing data were found for 2-methyl-1,3-butadiene and carbon disulfide. These differences may result from the quantitative methods used, poor precision in the analytical systems, retention volume correction factors, or combinations thereof.
- NASA/JSC reported the presence of selected siloxanes such as octamethylcyclotetrasiloxane. These compounds were observed consistently in samples but not in system blanks analyzed between sample runs. Boeing detected selected siloxanes at low concentrations, with the highest concentration being exhibited in system blanks, ground control samples, and *Mir* samples. The Boeing concentrations and relative ratios of concentrations were comparable for all blanks, controls, and *Mir* samples. Boeing data suggest a common system source and it could not be determined that the siloxanes were actually present in the samples.

### 5.3 Overall Assessment of Analytical Results

Considering the very different sampling and analysis procedures employed for *Mir 17*, much of the data reported by the laboratories are in good agreement. General trends in relative concentrations for different compounds and compound classes are in agreement. Variation within those trends are generally within a factor of 2 to 3. This variation is not surprising considering the methodological differences. The largest variations can generally be explained.

Differences between using grab sampling and time-integrated sampling techniques may account for some differences because time-integrated sampling may dilute concentration peaks that grab sampling may show. Analytical results for compounds that are poorly retained by Tenax are only semi-quantitative; therefore, some of the difference from grab-sample results for these compounds may be attributed to sampling methodology. Other physical factors must also be considered. For instance, the inlet to the SSAS became partially blocked during its operation. The time that this blockage occurred is unknown and its impact on the analytical results cannot be readily quantified; however, the comparison to IMBP sorbent tube results indicates that little effect was observed.

Given the results of data comparisons and the differing sampling and analytical approaches used, it can be concluded that the data obtained by the laboratories agree within their expected methodological uncertainty.

## 6.0 RECOMMENDATIONS FOR AIR QUALITY STUDIES ON BOARD *MIR*

A comprehensive plan to assess *Mir* air quality was developed during a meeting in Houston, TX in October–November 1995. This plan, which was formulated by toxicologists, chemists, and engineers of the Environmental Subgroup of Medical Working Group 8 of the *ISS* Program, builds upon the experience gained by the sampling conducted during *Mir* 17–19 summarized in table 2. Detailed results of these experiments are documented by references 1, 4, 23, and 24.

TABLE 2.—*Atmospheric sampling conducted on board Mir through expedition 19.*

Mission	Sampler	Sample Date	Number of Samples and Location	Comments
<i>Mir</i> 17	NASA SSAS	2/21/95 2/24/95 2/27/95 3/2/95 3/6/95 3/10/95 3/13/95	One SSAS tube each sampling day collected at the <i>Mir</i> base unit central control post	Each SSAS tube collected over a 24-hr period
	Boeing GSC	3/11/95 3/13/95 3/15/95	3 GSC samples/central control post 3 GSC samples/central control post 2 GSC samples/central control post	1 GSC collected on 3/11/95 and 3/13/95 provided to IMBP for analysis
	IMBP AK-1	3/11/95 3/13/95 3/15/95	2 tubes/central control post 2 tubes/central control post 2 tubes/central control post	1 sorbent tube collected on 3/11/95 and 3/13/95 provided to Boeing for analysis
<i>Mir</i> 18	NASA SSAS	3/21/95 3/29/95 4/10/95 4/30/95 5/15/95 6/4/95 6/29/95	1 SSAS tube each sampling day collected at the <i>Mir</i> base unit central control post	Each SSAS tube collected over a 24-hr period  Samples invalidated due to an obstruction of the SSAS inlet
	NASA GSC	3/21/95 3/29/95 4/10/95 4/30/95 5/15/95 5/29/95 6/4/95 6/12/95 6/29/95	At least 1 GSC sample each sampling day at the <i>Mir</i> base unit central control post	Samples collected within a 5-min span at various locations within the <i>Mir</i>  Samples collected on 6/12/95 were taken from 5 locations—all other samples were taken from the central control post



TABLE 2.—Atmospheric sampling conducted on board Mir through expedition 19 (continued).

Mission	Sampler	Sample Date	Number of Samples and Location	Comments
Mir 18	NASA Formaldehyde Monitors	3/22/95	1 personal sample collected each sampling day	Personal sampler worn for approximately 12 hr
		3/29/95		
		4/10/95		
		4/21/95		
		4/30/95		
		5/10/95		
		5/23/95		
6/12/95				
6/20/95				
Mir 19	NASA SSAS	7/7/95	1 SSAS tube each sampling day collected at the <i>Mir</i> base unit central control post	Each SSAS tube collected over a 24-hr period
		7/24/95		
		8/5/95		
		8/12/95		
		8/18/95		
		8/31/95		
	11/11/95			
	NASA GSC	7/26/95	1 GSC sample each sampling day at the <i>Mir</i> base unit central control post	3 samples collected simultaneously with Boeing and IMBP samples on 8/4/95, 8/17/95, and 9/7/95
		8/4/95		
		8/17/95		
		8/30/95		
		9/7/95		
		10/26/95		
		11/6/95		
	11/13/95			
NASA Formaldehyde Monitors	7/6/95	2 personal samples collected each sampling day	Personal samplers worn by cosmonauts for approximately 12 hr	
	7/23/95			
	8/4/95			
	9/8/95			
Boeing GSC	8/4/95	2 GSC samples collected each sampling day at the <i>Mir</i> base unit central control post	Samples collected simultaneously with NASA and IMBP samples	
	8/17/95			
	9/7/95			
IMBP AK-1	8/4/95	2 sorbent grab samples collected each sampling day at the <i>Mir</i> base unit central control post	Samples collected simultaneously with NASA and Boeing samples—2 tubes provided for NASA analysis	
	8/17/95			
	9/7/95			

The air quality study plan includes a basic program designed to address the majority of toxicological and engineering concerns and a “new analyses” program designed to determine whether the basic program overlooks certain compounds. The data provided by this plan will answer industrial hygiene, crew health, and engineering questions associated with the design and operation of the *ISS*. Toxicological and engineering rationales are given below for both the basic program and the new analyses program.

Equipment to be used during these studies reflects the inherent complementary nature of the various sampling and analytical methodologies. Information provided in sections 3 and 4 demonstrates that grab sampling canister and sorbent tube sampling methods provide broad coverage for the entire range of contaminants routinely observed in spacecraft cabin air. The canister sampling method provides more reliable results for highly volatile compounds, while the sorbent tube sampling method provides more reliable results for polar and heavy nonpolar organic compounds. In combination with formaldehyde sampling, these methods provide the appropriate data to assess spacecraft cabin air quality.

In order to implement this plan, the safety, reliability, and QA certification processes discussed in section 3 require careful coordination between NASA and its Russian counterparts. This is necessary since both parties are involved in certifying and inspecting hardware, developing training manuals and videos, developing joint procedures and timelines for hardware use during the *Mir* missions, and training astronauts and cosmonauts.

### **6.1 Basic Program of Cabin Air Quality Studies**

The basic cabin air sampling program for *Mir* 21–24 is outlined in tables 3 and 4. All NASA/JSC SSAS and grab-sample canisters will be analyzed by the NASA/JSC Toxicology Laboratory according to methods that were summarized in section 4.0. Most of the IMBP AK–1 samples will be analyzed in the IMBP laboratories; however, one exposed sampler and one blank sampler will be provided to NASA/JSC for analysis by their sampling methods. The capability to sample highly volatile compounds over a period of a few days needs to be investigated. Data on possible methods to achieve this capability need to be collected and compared to determine which method to pursue for spacecraft cabin air sampling. The basic plan also includes passive sampling for formaldehyde by badges that have already been used on board the shuttle and during *Mir* 18–19. These badges have minimum airflow velocity requirements. As previously noted, a recent study comparing results from these badges with those from an airflow-independent method have verified the accuracy of the basic method on the ground. The desired sensitivity of the formaldehyde detection system should be about one-tenth of the long-term SMAC of 0.05 mg/m<sup>3</sup>. At this time, five area samplers, five personal samplers, and two in-flight controls for formaldehyde have been manifested for NASA 2 and 3 (*Mir* 21–22). For NASA 4 and 5 (*Mir* 22–24), 10 area samplers and 10 personal samplers each, along with in-flight controls, are manifested.

The toxicological and engineering rationale summarized in section 2.0 centers on the diverse and dynamic sources of air contaminants and the complex removal processes on board spacecraft. The basic method must be able to characterize the nominal air contaminants to provide data for toxicological assessment of long-term crew exposures and for verification of engineering designs, ECLSS operation, and safety margins. Both toxicologists and engineers have strong interests in spatial variations (concentration gradients) of air contaminants; hence, the basic plan includes samples obtained simultaneously from diverse locations within the *Mir*. Time-integrated samples are the most useful for assessing nominal air contaminants.

TABLE 3.—Mir 21–24 basic sampling program.

Launch Vehicle	Sampler	Number	Mission	Sampling Day	Number of Samples and Location	Return Vehicle	Comments
STS-74	SSAS	1	Mir 21	6 31 59 87	1 SSAS tube at the central control post each sampling day	STS-76	1. All SSAS samples for Mir 21 are in the Mir base unit
STS-74	GSC	6	Mir 21	6 31 59 87	1 GSC at the central control post each sampling day	STS-76	1. 2 GSC units for contingency samples 2. All GSC samples for Mir 21 are in the Mir base unit
STS-76	SSAS	2	NASA 2 (Mir 21–22)	10 30 60 90 130	1 SSAS tube at the central control post and 1 SSAS tube at a second location each sampling day	STS-79	1. SSAS units remain in their specified locations for the entire mission
STS-76	GSC	12	NASA 2 (Mir 21–22)	30 60 90 130	1 GSC at the central control post each sampling day; 4 GSC's at remote locations on 1 day; 4 GSC's during return vehicle docked phase	STS-79	1. 4 GSC units for contingency samples
STS-79	SSAS	2	NASA 3 (Mir 22)	10 30 60 90 130	1 SSAS tube at the central control post and 1 SSAS tube at a second location each sampling day	STS-81	1. SSAS units remain in their specified locations for the entire mission
STS-79	GSC	12	NASA 3 (Mir 22)	30 60 90 130	1 GSC at the central control post each sampling day; 4 GSC's at remote locations on 1 day; 4 GSC's during return vehicle docked phase	STS-81	1. 4 GSC units for contingency samples
STS-81	SSAS	2	NASA 4 (Mir 22–23)	10 30 60 90 130	1 SSAS tube at the central control post and 1 SSAS tube at a second location each sampling day	STS-84	1. SSAS units remain in their specified locations for the entire mission
STS-81	GSC	12	NASA 4 (Mir 22–23)	30 60 90 130	1 GSC at the central control post each sampling day; 4 GSC's at remote locations on 1 day; 4 GSC's during return vehicle docked phase	STS-84	1. 4 GSC units for contingency samples
STS-84	SSAS	2	NASA 5 (Mir 23–24)	10 30 60 90 130	1 SSAS tube at the central control post and 1 SSAS tube at a second location each sampling day	STS-86	1. SSAS units remain in their specified locations for the entire mission
STS-84	GSC	12	NASA 5 (Mir 23–24)	30 60 90 130	1 GSC at the central control post each sampling day; 4 GSC's at remote locations on 1 day; 4 GSC's during return vehicle docked phase	STS-86	1. 4 GSC units for contingency samples

TABLE 4.—Sampling schedule for Mir 21–24

Mission	Sampler	Mission Sample Day	Number of Samples and Location						Comments
			Base Unit	Kvant	Kvant-2	Crystal	Spektr	Pritroda	
Mir 21	NASA SSAS	6	1	0	0	0	0	0	1. Investigate reference point concentrations in base unit 2. Provisions for sample exchange between NASA and IMBP 3. Two GSC's remaining for contingency  1. Collect samples at reference point in base unit 2. Collect second set of SSAS samples in Pritroda to study new hardware offgassing 3. Spatial samples to investigate gradients after Pritroda docking 4. Provisions for sample exchange between NASA and IMBP 5. Four GSC's remaining for contingency or for sampling during and after shuttle docking* 6. Five additional formaldehyde monitors are deployed as personal samplers. Two flight control monitors are also provided.
		31	1	0	0	0	0	0	
		59	1	0	0	0	0	0	
		87	1	0	0	0	0	0	
	6	1	0	0	0	0	0		
	31	1	0	0	0	0	0		
	59	1	0	0	0	0	0		
	87	1	0	0	0	0	0		
	6	1	0	0	0	0	0		
	31	1	0	0	0	0	0		
59	1	0	0	0	0	0			
87	1	0	0	0	0	0			
NASA 2 (Mir 21–22)	NASA SSAS	10	1	0	0	0	0	0	1. Collect samples at reference point in base unit 2. Collect second set of SSAS samples in Pritroda to study new hardware offgassing 3. Spatial samples to investigate gradients after Pritroda docking 4. Provisions for sample exchange between NASA and IMBP 5. Four GSC's remaining for contingency or for sampling during and after shuttle docking* 6. Five additional formaldehyde monitors are deployed as personal samplers. Two flight control monitors are also provided.
		30	1	0	0	0	0	0	
		60	1	0	0	0	0	0	
		90	1	0	0	0	0	0	
	130	1	0	0	0	0	0		
	30	1	0	1	1	1	1		
	60	1	0	0	0	0	0		
	90	1	0	0	0	0	0		
	130	1	0	0	0	0	0		
	10	1	0	0	0	0	0		
30	1	0	0	0	0	0			
60	1	0	0	0	0	0			
90	1	0	0	0	0	0			
130	1	0	0	0	0	0			
NASA 2 (Mir 21–22)	NASA GSC	10	1	0	0	0	0	0	1. Collect samples at reference point in base unit 2. Collect second set of SSAS samples in Pritroda to study new hardware offgassing 3. Spatial samples to investigate gradients after Pritroda docking 4. Provisions for sample exchange between NASA and IMBP 5. Four GSC's remaining for contingency or for sampling during and after shuttle docking* 6. Five additional formaldehyde monitors are deployed as personal samplers. Two flight control monitors are also provided.
		30	1	0	0	0	0	0	
		60	1	0	0	0	0	0	
		90	1	0	0	0	0	0	
	130	1	0	0	0	0	0		
	30	1	0	1	1	1	1		
	60	1	0	0	0	0	0		
	90	1	0	0	0	0	0		
	130	1	0	0	0	0	0		
	10	1	0	0	0	0	0		
30	1	0	0	0	0	0			
60	1	0	0	0	0	0			
90	1	0	0	0	0	0			
130	1	0	0	0	0	0			
NASA 2 (Mir 21–22)	NASA Formaldehyde Monitors	10	1	0	0	0	0	0	1. Collect samples at reference point in base unit 2. Collect second set of SSAS samples in Pritroda to study new hardware offgassing 3. Spatial samples to investigate gradients after Pritroda docking 4. Provisions for sample exchange between NASA and IMBP 5. Four GSC's remaining for contingency or for sampling during and after shuttle docking* 6. Five additional formaldehyde monitors are deployed as personal samplers. Two flight control monitors are also provided.
		30	1	0	0	0	0	0	
		60	1	0	0	0	0	0	
		90	1	0	0	0	0	0	
	130	1	0	0	0	0	0		
	30	1	0	1	1	1	1		
	60	1	0	0	0	0	0		
	90	1	0	0	0	0	0		
	130	1	0	0	0	0	0		
	10	1	0	0	0	0	0		
30	1	0	0	0	0	0			
60	1	0	0	0	0	0			
90	1	0	0	0	0	0			
130	1	0	0	0	0	0			
NASA 2 (Mir 21–22)	IMBP AK-1	10	1	0	0	0	0	0	1. Collect samples at reference point in base unit 2. Collect second set of SSAS samples in Pritroda to study new hardware offgassing 3. Spatial samples to investigate gradients after Pritroda docking 4. Provisions for sample exchange between NASA and IMBP 5. Four GSC's remaining for contingency or for sampling during and after shuttle docking* 6. Five additional formaldehyde monitors are deployed as personal samplers. Two flight control monitors are also provided.
		30	1	0	0	0	0	0	
		60	1	0	0	0	0	0	
		90	1	0	0	0	0	0	
	130	1	0	0	0	0	0		
	30	1	0	1	1	1	1		
	60	1	0	0	0	0	0		
	90	1	0	0	0	0	0		
	130	1	0	0	0	0	0		
	10	1	0	0	0	0	0		
30	1	0	0	0	0	0			
60	1	0	0	0	0	0			
90	1	0	0	0	0	0			
130	1	0	0	0	0	0			

TABLE 4.—Sampling schedule for Mir 21–24 (continued).

Mission	Sampler	Mission Sample Day	Number of Samples and Location						Comments
			Base Unit	Kvant	Kvant-2	Crystal	Spektr	Priroda	
NASA 3 (Mir 22)	NASA SSAS	10	1	0	0	0	0	1	<ol style="list-style-type: none"> <li>1. Collect samples at reference point in base unit</li> <li>2. Collect second set of SSAS samples in Spektr to study offgassing from U.S./Russian hardware complement</li> <li>3. Spatial samples early in mission to investigate gradients</li> <li>4. Provisions for sample exchange between NASA and IMBP</li> <li>5. Four GSC's remaining for contingency or for sampling during and after shuttle docking</li> <li>6. Five additional formaldehyde monitors are deployed as personal samplers. Two flight control monitors are also provided.</li> </ol>
		30	1	0	0	0	0	1	
		60	1	0	0	0	0	1	
	NASA GSC	90	1	0	0	0	0	1	
		130	1	0	0	0	0	1	
		30	1	0	0	0	0	0	
	NASA GSC	60	1	1	1	1	1	1	
		90	1	0	0	0	0	0	
		130	1	0	0	0	0	0	
	NASA Formaldehyde Monitors	10**	1	0	0	0	0	0	
		30**	1	0	0	0	0	0	
		60**	1	0	0	0	0	0	
	IMBP AK-1	90**	1	0	0	0	0	0	
130**		1	0	0	0	0	0		
30		1	0	0	0	0	0		
NASA 4 (Mir 22-23)	NASA SSAS	60	1	1	1	1	1	1	<ol style="list-style-type: none"> <li>1. Collect samples at reference point in base unit</li> <li>2. Collect second set of SSAS samples in Crystal to study offgassing from experimental hardware complement</li> <li>3. Spatial samples midmission to investigate gradients</li> <li>4. Provisions for sample exchange between NASA and IMBP</li> <li>5. Four GSC's remaining for contingency or for sampling during and after shuttle docking</li> <li>6. Ten additional formaldehyde monitors are deployed as personal samplers. Flight control monitors are also provided.</li> </ol>
		90	1	0	0	0	0	0	
		130	1	0	0	0	0	0	
	NASA GSC	10	1	0	0	1	1	0	
		30	1	0	0	1	1	0	
		60	1	0	0	1	1	0	
	NASA GSC	90	1	0	0	1	1	0	
		130	1	0	1	1	1	1	
		30	1	0	0	0	0	0	
	NASA Formaldehyde Monitors	60	1	0	0	0	0	0	
		90	1	0	0	0	0	0	
		130	1	0	0	0	0	0	
	IMBP AK-1	30	1	0	0	0	0	0	
60		1	0	0	0	0	0		
90		1	0	0	0	0	0		
IMBP AK-1	130	1	0	0	0	0	0		

TABLE 4.—Sampling schedule for Mir 21–24 (continued).

Mission	Sampler	Mission Sample Day	Number Of Samples And Location					Comments	
			Base Unit	Kvant	Kvant-2	Crystal	Spektr		Priroda
NASA 5 (Mir 23–24)	NASA SSAS	10	1	0	1	0	0	0	1. Collect samples at reference point in base unit 2. Collect second set of SSAS samples in Kvant-2 3. Spatial samples late in mission to investigate gradients 4. Provisions for sample exchange between NASA and IMBP 5. Four GSC's remaining for contingency or for sampling during and after shuttle docking 6. Ten additional formaldehyde monitors are deployed as personal samplers. Flight control monitors are also provided.
		30	1	0	1	0	0	0	
		60	1	0	1	0	0	0	
	NASA GSC	90	1	0	1	0	0	0	
		130	1	0	1	0	0	0	
		30	1	0	0	0	0	0	
	NASA Formaldehyde Monitors	60	1	0	0	0	0	0	
		90	1	0	0	0	0	0	
		130	1	1	1	1	1	0	
		10**	2	0	0	0	0	0	
	IMBP AK-1	30**	2	0	0	0	0	0	
		60**	2	0	0	0	0	0	
		90**	2	0	0	0	0	0	
130**		2	0	0	0	0	0		
Total Number of Samples		94	4	13	13	13	9	146 total samples (36 by IMBP)***	

\* Sampling at shuttle docking where time, T = 0 at hatch opening and samples taken at T = -0.5, +0.5, +2, and +12 hr. Sampling location is at the central control post or in the module connected directly to the shuttle.

\*\* When possible, formaldehyde monitoring will be scheduled when a crew member plans to use formaldehyde-containing fixatives.

\*\*\* Add an additional 30 personal formaldehyde samples for a grand total of 176.

The basic plan also addresses the interests of toxicologists and engineers in transient processes that result in increases in certain pollutant concentrations. Results from *Mir* flights have already identified transients of Freon™ 82, thought to be associated with opening newly-arrived modules and ethylene glycol possibly associated with leakage from thermal control systems. It is very important for toxicologists to know the extent of crew exposure to pollutants generated by transient sources, and it is important for engineers to know how the contamination control system handles the unexpected load. It is extremely important to both toxicologists and engineers that experimentally-validated models be available to predict the rate at which transient contamination is removed from air in the event of an accidental release of a known compound. To some extent, data from the basic plan can provide partial validation of these models. Furthermore, when air data are combined with data from humidity condensate and cabin leak rate, it is possible, in principle, to calculate a cabin mass balance for trace contaminants. By subtracting an estimate of the human contribution, the contaminant production rate from hardware offgassing can be estimated. This information is useful in defining contaminant loads that the contamination control system must be engineered to handle.

Contingency air samplers have been made available as part of the basic plan so that the crew can sample air if they suspect an unusual contamination problem. If the samplers are not used for contingencies, then they can be used to study the dynamics of air contaminants as they mix after hatch opening and crew exchange. The proposed plan would involve grab samples at distal locations on both sides of a hatch, opened at time equal to zero and sampled at time equal to -0.5, +0.5, +2.0, and +12 hr. This sequence could be followed when the shuttle docks with the *Mir* during STS-84 and STS-86. Four grab-sample containers would need to be manifested on the shuttle to support sampling on that side of the hatch. Appropriate distal locations for sampling would be the shuttle middeck and the *Mir* central command post.

## **6.2 Potential New Air Monitoring Efforts**

Although the basic plan is thorough, it may not be able to provide quantitative data on certain important contaminants. Criteria adopted by the Environmental Subgroup to determine whether new methods should be used to improve the scope air quality assessments are the following:

- Assess the basic sampling and analytical methods presently in use to determine if they can accurately quantify the substance; if not, identify new methods.
- Plausible sources of the contaminant are present on board the spacecraft.
- Agreement can be reached on detection limits of interest.
- Analytical methods suitable for spacecraft are available.
- Ground-based testing cannot adequately address the contaminant questions.

Using the second of these criteria, plausible sources, the proposed new contaminants were reviewed according to the following sections.

### **6.2.1 Contaminants Generated by Human Metabolism**

Contaminants that are generated by human metabolism but are not well characterized by the basic program include ammonia, volatile amines, and volatile fatty acids. Ammonia, which cannot be quantified by the basic methods, is important because it is a key engineering design “driver” for the

activated charcoal bed in the Trace Contaminant Control Subassembly for the U.S. segment of the *ISS*. A major function of this bed is to prevent ammonia from reaching the high-temperature oxidizer, where it could be converted to highly toxic oxides of nitrogen. A method for ammonia must be developed and have a sensitivity to 0.3 mg/m<sup>3</sup>.

Volatile amines need to be measured at detection limits of 0.3 mg/m<sup>3</sup> or better. Sorbent trap methods exist for these contaminants; however, the basic methods need to be evaluated for their ability to quantify volatile amines.

Volatile fatty acids originate from human perspiration and respiration and can cause strong odors in spacecraft air. Crews adapt to these odors; however, during crew exchanges the odors can be noxious until adaptation occurs. These are basic methods to quantify many of the volatile fatty acids; however, it must be determined if some important members of this group cannot be measured by the basic methods. The detection limit for these compounds should be  $\leq 0.5$  mg/m<sup>3</sup>.

### **6.2.2 Contaminants Generated by Motors, Electronic Devices, and Catalytic Beds**

Contaminants that can potentially be generated by motors, electronic devices, and catalytic beds include nitrogen dioxide and ozone. Since these highly toxic contaminants originate from hardware rather than humans, they can be evaluated during unmanned ground-based testing to determine the need for in-flight sampling. To determine a need, nitrogen dioxide and ozone production must be investigated during *ISS* life support systems tests. If it is determined that in-flight sampling is necessary, the nitrogen dioxide and ozone methods would have to be developed having a sensitivity of 0.05 mg/m<sup>3</sup> and 0.02 mg/m<sup>3</sup>, respectively.

### **6.2.3 Contaminants From Combustion of Nonmetallic Materials**

Hydrogen fluoride, hydrogen chloride, and hydrogen cyanide can be produced by burning non-metallic materials. These contaminants would not normally be a part of spacecraft cabin air; however, they could be generated suddenly by combustion of wire insulation, electronic circuit boards and components, and other electrical devices. Real-time monitoring for these highly toxic contaminants is preferred over sorbent methods that depend on postflight analysis. The method detection limit should be 0.5 to 1.0 mg/m<sup>3</sup> to deal with accidental releases. Continued development of a combustion products analyzer for spacecraft is recommended.

### **6.2.4 Contaminants Originating From Multiple Sources**

Aliphatic aldehydes result from incomplete oxidation of alcohols, human metabolism, hardware offgassing, and food preparation. Except for formaldehyde, the basic methods can be used to quantify important members of this class of compounds. As described previously, supplementary methods such as formaldehyde badges may be appropriate.



## 7.0 CONCLUSIONS ON AIR QUALITY ASSESSMENT METHODOLOGY

Conclusions that can be made based upon the information presented on the available sampling and analysis methods for conducting spacecraft air quality assessment are the following:

- The sampling methods available to both the U.S. and Russian sides are, for the most part, acceptable for use in the study of the *Mir* and *ISS* cabin air quality.
- The sampling methods using canisters and sorbents are complementary for many compounds because of different selectivities for specific classes of organic compounds.
- Given the available analytical results, the amount of water used when preparing grab sample canisters for use is an unresolved issue.
- The analytical methods available are, for the most part, capable of meeting toxicological requirements for sensitivity and accuracy of measurements.
- The basic program for cabin air sampling on board the *Mir* and *ISS* is directed at both toxicological and engineering goals and concerns.
- The sampling methods available may require supplementation to monitor some classes of compounds that are both toxicological and engineering concerns.

## **8.0 RECOMMENDATIONS ON AIR QUALITY ASSESSMENT METHODOLOGY**

Based upon the information presented on sampling methods, analytical methods, and toxicological and engineering considerations, recommendations on the air quality assessment methodology to be used on board the *Mir* station and the *ISS* are the following:

- A means should be provided to minimize the risk of inlet clogging when collecting long-term cabin air samples.
- Results for compounds that are poorly retained by Tenax beds should be reported as semiquantitative for information only.
- Analytical surrogates with different analytical properties should be used whenever possible to increase precision of the sample analysis.
- Additional measures should be taken to provide a reliable seal for the short-term sorbent tubes.
- Formaldehyde measurements with the badge method should continue and should be confirmed by a flow-independent sampling method.

## **9.0 RECOMMENDATIONS FOR U.S./RUSSIAN COOPERATION**

Studying the air quality on board both the *Mir* station and the *ISS* will require coordination between toxicologists, chemists, engineers, and many others to ensure a successful program. Recommendations that promote the achievement of the desired results are the following:

- The basic program presented for sampling on board the *Mir* should be implemented.
- Careful coordination between U.S. and Russian experts should continue.
- NASA should consider the need for supplementing the basic archival sampling program according to the principles and needs specified in section 6.2.
- Toxicologists, chemists, and engineers on the U.S. and Russian sides should coordinate their work via the Environmental Subgroup of Medical Working Group 8 to extend the *Mir* archival sampling program to the *ISS* in order to complement baselined near-real-time analyzers.

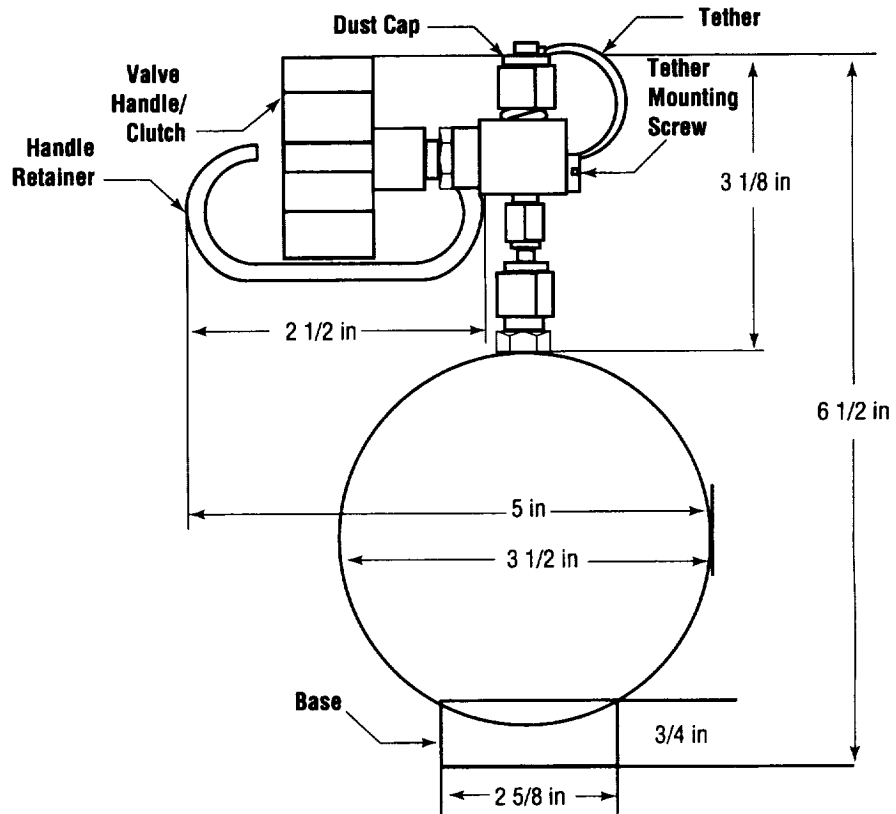
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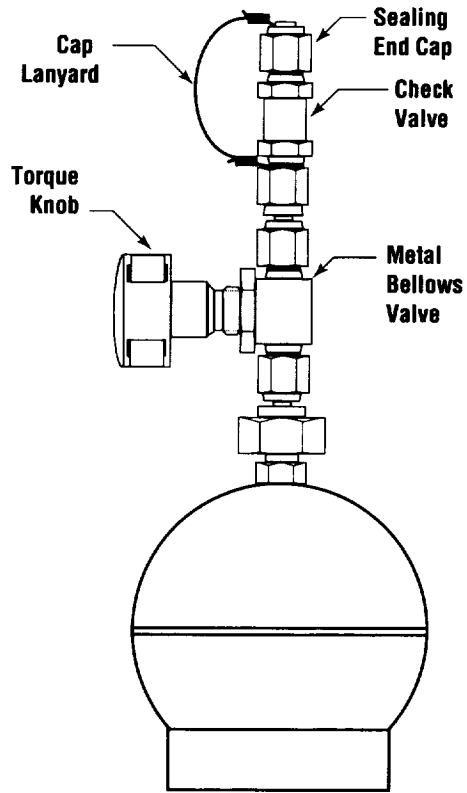
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**APPENDIX A  
GRAB SAMPLER SCHEMATICS**

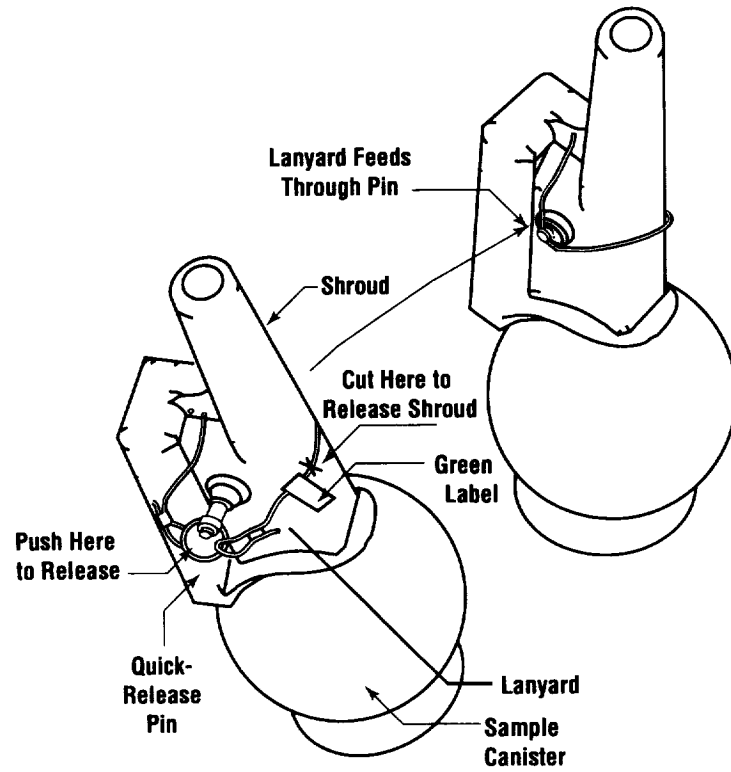
**NASA/JSC Flight Grab Sample Container**



**Summa™-Passivated Canister**



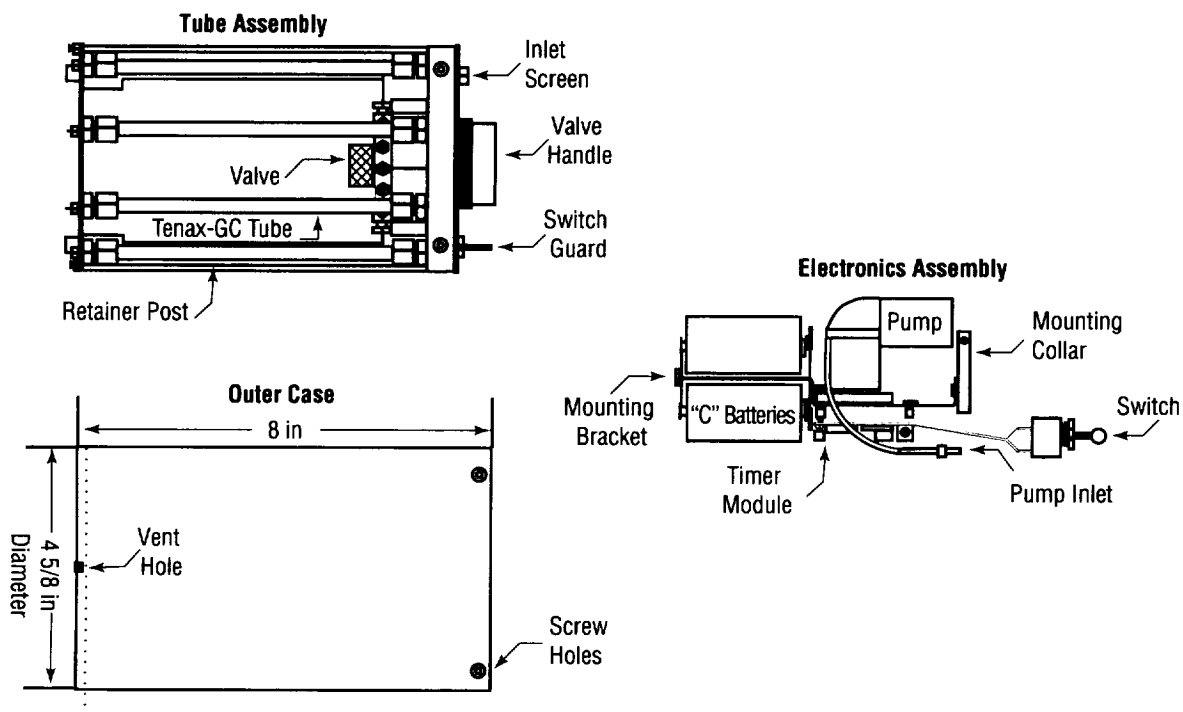
**Canister With Protective Shroud and Custody Seal**





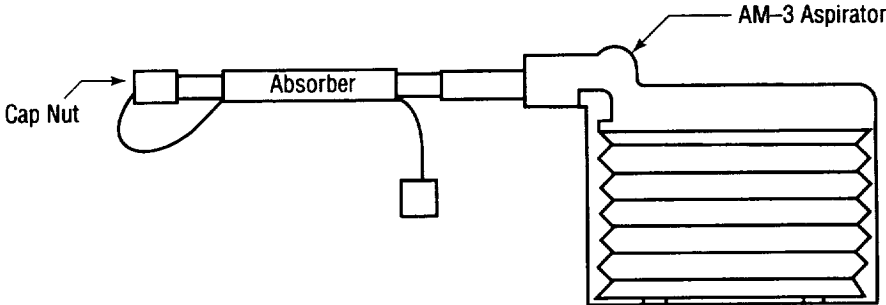
## APPENDIX B SOLID SORBENT AIR SAMPLER SCHEMATICS

NASA/JSC Diagram of Solid Sorbent Air Sampler



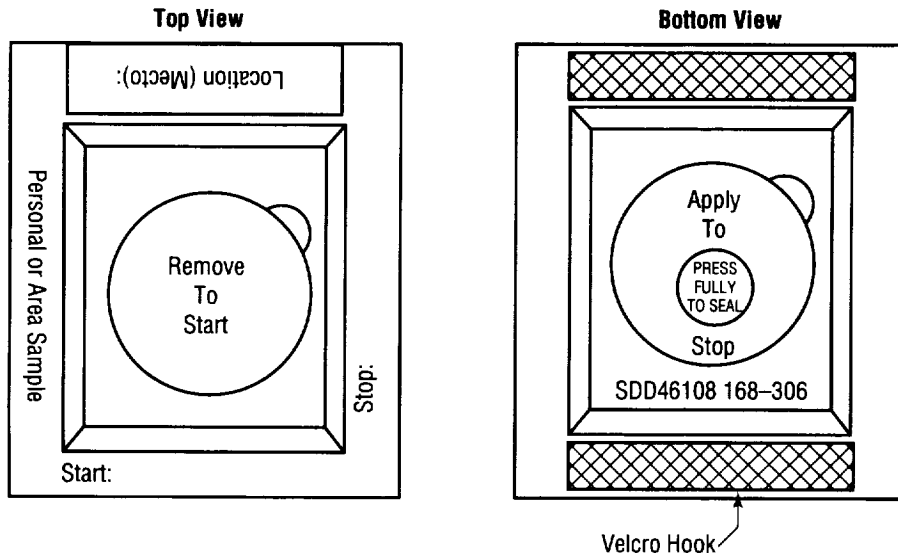
**APPENDIX C**  
**IMBP SOLID SORBENT SAMPLER SCHEMATIC**

**Diagram of Portable, Onboard Sampler**



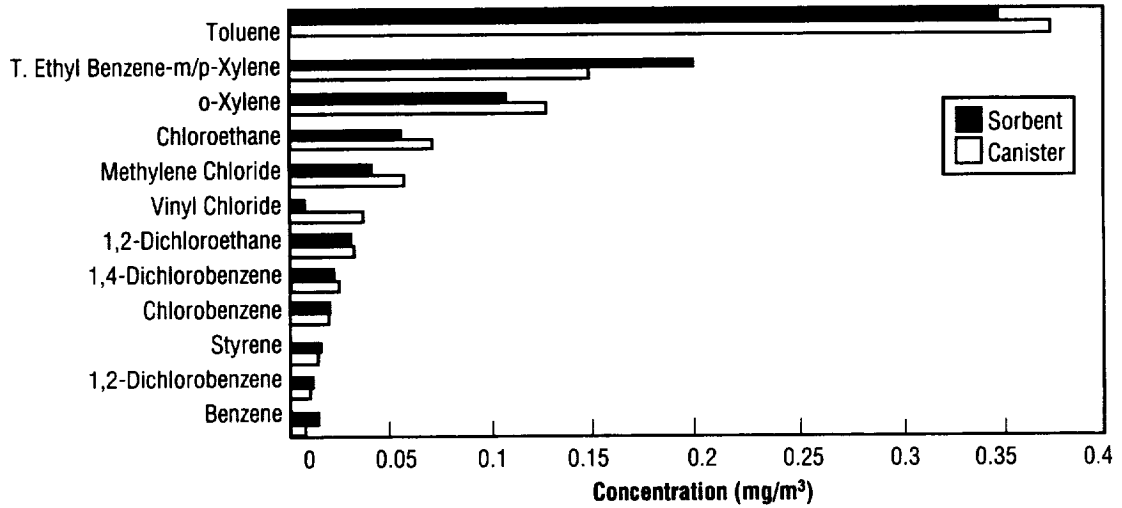
**APPENDIX D  
FORMALDEHYDE SAMPLER SCHEMATIC**

**Formaldehyde Badge Sampler**

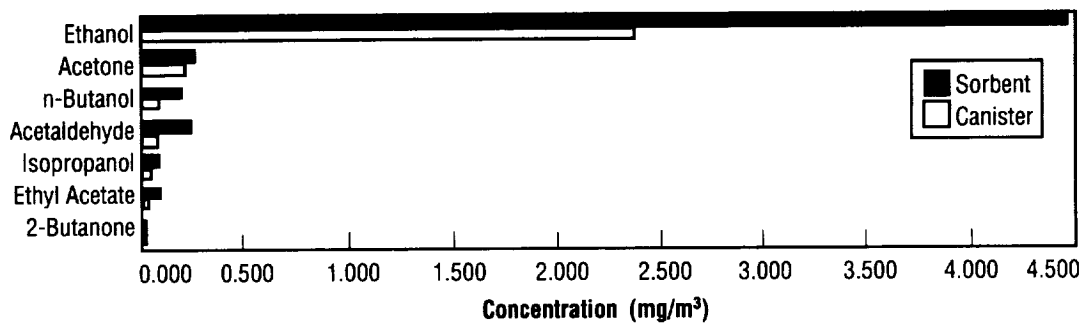


## APPENDIX E TENAX VERSUS CANISTER BIAS DATA

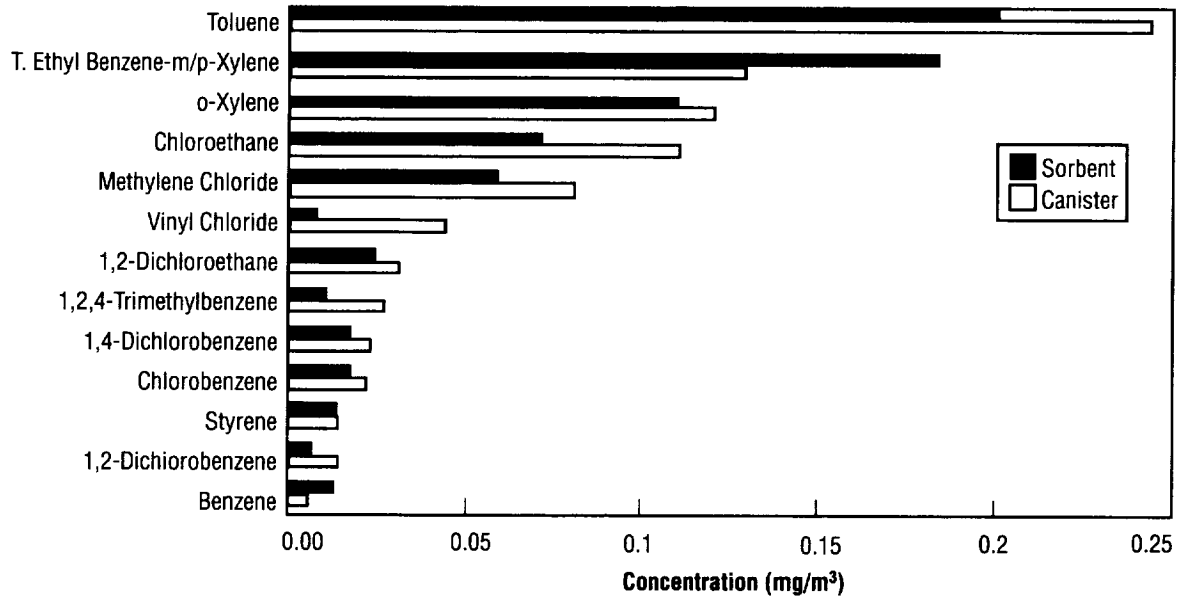
Comparison of canister and sorbent tube data sampling event 1 (TO-14 Compounds)



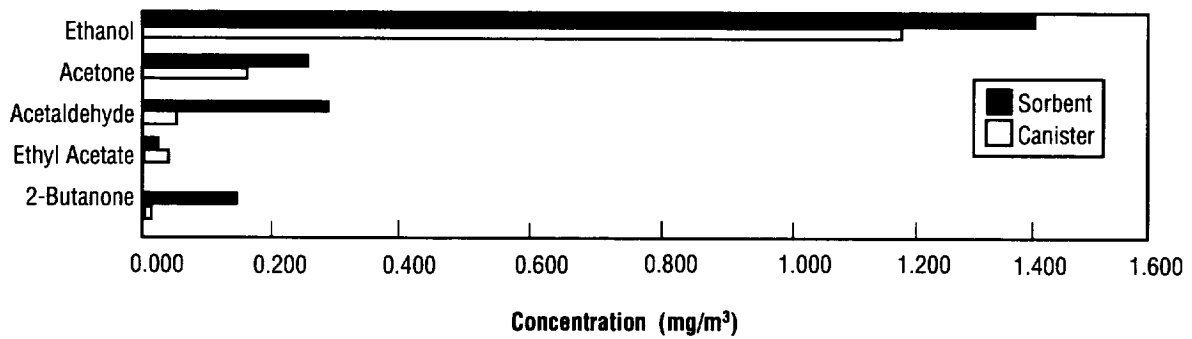
Comparison of canister and sorbent tube data sampling event 1 (polar organics)



Comparison of canister and sorbent tube data sampling event 2 (TO-14 Compounds)



Comparison of canister and sorbent tube data sampling event 2 (polar organics)



**APPENDIX F**  
**TENAX RETENTION VOLUME ADJUSTMENT DATA**

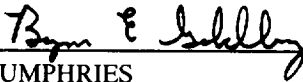
<b>Compound</b>	<b>Correction Factor</b>
Dichlorodifluoromethane	46
Chloromethane	4.6
Methanol	10.5
Acetaldehyde	3.1
Ethanol	2.8
Chloroethane	4.6
Trichlorofluoromethane	12.3
2-methyl-2-propanol	5.2
1,1-dichloroethene	1.8
Dichloromethane	1.4
1,1,2-trichloro-1,2,2-trifluoroethane	10.2
1-chloro-2-fluoroethane	12.3
2-methyl-1,3-butadiene	3.7
Carbon disulfide	74

## APPROVAL

### **RATIONALE AND METHODS FOR ARCHIVAL SAMPLING AND ANALYSIS OF ATMOSPHERIC TRACE CHEMICAL CONTAMINANTS ON BOARD *MIR* AND RECOMMENDATIONS FOR THE *INTERNATIONAL SPACE STATION***

J.L. Perry, J.T. James, H.E. Cole, T.F. Limero, and S.W. Beck

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.



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W.R. HUMPHRIES

Director, Structures and Dynamics Laboratory

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