TOXICOLOGICAL INVESTIGATION OF MIR AIR DURING NASA 3
(October 1996 to January 1997)

Principle Investigator: John T. James, Ph.D
NASA-JSC
Medical Operations Branch
Houston, TX 77058

Co-Investigators: Thomas F. Limero, Ph.D.
Steve W. Beck, M.S.
Lilly Yang, Ph.D.
Millie P. Martin, B.S.
Marilyn L. Matney, Ph.D.
Phillip A. Covington, B.S.
John F. Boyd, M.S.
Debra A. W. Lind, M.S.

THIS DOCUMENT MUST BE DISCLOSED ONLY TO U.S. AND RUSSIAN PERSONNEL DIRECTLY SUPPORTING MANNED SPACEFLIGHT

July1997

TOXICOLOGICAL ASSESSMENT OF MIR AIR DURING NASA 3

1. Introduction

Crew members aboard spacecraft are exposed continuously to pollutants in the respirable air. These pollutants originate from materials offgassing, systems leaks, use of utility chemicals, payload leaks, human metabolism, and microbial metabolism. If pollutant concentrations reach high levels, the crew can experience disturbances in cardiac rhythms, eye and respiratory irritation, headache and disorientation, and be at higher risk for development of chronic disease (e.g. cancer). Furthermore, excessive air pollution can confound biomedical experiments conducted aboard the spacecraft.

1.1 Hypotheses to be Tested

Mir air will meet NASA's standards for crew health during long-term exposure of astronauts to trace contaminants. The standards are specified in JSC 20584.

The mixing time required for air contaminants to reach a steady state will be less than 6 hours after hatch opening between the Mir and Shuttle.

Spatial variations in contaminant concentrations inside the Mir complex will be small (<25%).

A comparison of the three methods used for general air sampling will show that the methods are comparable for most contaminants. These methods include the U.S. grab sample canisters (GSCs), the U.S. solid sorbent air sampler (SSAS), and the Russian AK-1 sorbent sampler.

1.2 Objectives of the Experiment

Our primary objective was to periodically sample Mir air at various locations in the complex to estimate the effect of airborne pollutants on crew health. Samples were analyzed in the NASA-JSC Toxicology Laboratory and the results compared to NASA standards for air quality during long-term missions.

Secondary objectives were to assess the rate of pollutant mixing when the Shuttle hatch is opened in the docked phase. There are specific pollutants that accumulate in Mir or in Shuttle air and can be observed to redistribute or be diluted after hatch opening between the two spacecraft. Another objective was comparison of 5 samples taken simultaneously from different locations within the complex. Finally, samples were taken concurrently using 3 different types of sampler to compare the similarity of sampling methods.

1.3 Background and History of the Project

The goal of the effort is to determine whether the crew has been exposed to concentrations of air pollutants that could pose a health threat. The planning for these investigations has been the subject of several meetings of the Environments Subgroup of Medical Working Group 8 (1,2) and a report on the various sampling methods and analytical approaches has been published (3). In past Shuttle and Mir missions, formaldehyde concentrations have exceeded NASA's spacecraft maximum allowable concentrations (SMACs). Data from Mir 19 suggested that periodic releases of this irritant into the air may be occurring, and some experiments are believed to have leaked formaldehyde during the Mir 18 flight (4,5). During NASA 2, many of the formaldehyde measurements were above long-term exposure limits, hence, formaldehyde was a major component of the irritant toxicity group (6). In addition, spikes of some of the freons used in the coolant loops have been detected in the atmosphere (7). Early concerns about benzene in the Mir atmosphere have not been confirmed by more recent findings.

2. Research Methods and Operations

The process leading to toxicological assessment of spacecraft air can be broken into 4 steps. Preflight preparations of the sampling devices, except the AK-1 sampler, are conducted in the NASA-JSC Toxicology Laboratory to ensure that each sampler is clean and can perform as expected. In-flight activities consist of sample acquisition by crew members and appropriate labeling to indicate time and location of sample. After flight, the samplers are returned to the NASA-JSC Toxicology Laboratory for analysis according to laboratory standard operating procedures (SOPs). Once the analytical data are complete, the toxicologist reviews and assembles the data according to toxicological category, applies standard equations to determine air quality, and addresses each of the hypotheses.

2.1 Preflight Preparation of the Air Sampling Devices

Canister samplers of approximately 350 ml volume (Scientific Instrumentation Specialists, Moscow, ID) were obtained from the company with SUMMA electropolished interior surfaces. The canisters were maintained under controlled conditions during all steps of processing. The preflight preparations were conducted in the following sequence: 1) high vacuum leak check, 2) cleaning and proofing to 5 ppb by GC/MS for each target compound, 3) evacuation to $<10^{-5}$ torr, 4) addition of 10 ml of 1.51 ppm surrogate standards of acetone-13C, chlorobenzene-D5, and fluorobenzene-D5, and 5) labeling of samplers for use in flight.

The SSAS, built for NASA by Valco, Houston, TX, was prepared for flight as follows: 1) each of the 8 tubes was cleaned with ultrapure nitrogen at 250°C and proofed to 5 ppb, 2) each tube was dosed with 20 ml of the same surrogate mixture as used for the canisters, 3) fresh batteries were placed in the unit and the flow through each tube was measured in triplicate using a small volume of clean, humidified air, and 4) the unit was labeled for use during the mission.

Formaldehyde badges (model PF-20) were obtained from Air Quality Research, Research Triangle Park, NC. Preflight preparation involved the following steps: 1) independent determination of the formaldehyde uptake rate of at least 3 badges from each lot, 2) reconfiguration of the commercial badges to fit NASA flight configuration, 3) using a known formaldehyde vapor concentration to dose positive controls that fly with the sampling badges, and 4) packaging badges into kits of 12 badges (including positive controls and unexposed controls) for use during flight.

The Russian AK-1 sampler tubes (150 mm X 5 mm diameter (id) stainless steel) were prepared at IMBP in Moscow. The sorbent material (Tenax) was solvent rinsed and heated to 300°C before being packed into each tube. The sorbent tube was conditioned by passing inert gas through the tube at 300°C and then verifying that the sorbent was clean by analysis.

2.2 In flight Sampling of the Atmosphere

Canister “grab” samples were obtained by a crew member by removing the dust cover on the inlet, holding the canister away from the body, opening the valve for approximately 10 seconds, closing the valve, replacing the dust cap, and marking the time and place of sampling. The time-integrated SSAS samples were taken by turning the selector knob to the desired tube and turning on the unit power switch. Approximately 24 hours, later the power switch was turned off and the selector turned to the park position (position 8). The formaldehyde badge was used to obtain a personal sample or an area sample. The face cover was removed and the badge attached to the front of the crew member’s shirt or to a location near the command post with good air flow. At the end of the exposure period (approximately 12 hours for personal samples and 24 hours for area samples), the badge was removed and resealed by a crew member. AK-1 samples were taken by removal of the end caps, pumping 500 ml through the tube (5 strokes with a 100 ml bellows pump), and resealing the tube.

2.3 Post-flight Analyses of the Samples

Canister samplers were analyzed by GC and GC/MS according to standard operating procedures in the NASA/JSC Toxicology Laboratory. The GC/MS method is an adaptation of the U.S. EPA's TO-14 method; the primary adaptations being the inclusion of standards for the many polar compounds found in spacecraft air and a separate analysis for freon 82 and freon 218 using reduced trapping temperatures in the GC/MS inlet. Each SSAS tube was tested for flow after the flight, then thermally desorbed into 500 ml canisters similar to flight canisters except for volume. The canisters were then analyzed in the same way as flight canisters except that there were no GC analyses. Filters were removed from each of the formaldehyde badges and extracted with formaldehyde-free water. The aqueous extracts were analyzed for formaldehyde by a chromotropic acid-spectrophotometric method. The AK-1 tubes were thermally desorbed into 500 ml canisters. The canister contents were analyzed by GC/MS.

2.4 Toxicological Analyses of the Analytical Data

Toxicological analysis of the analytical concentration data consists of looking at the combined effects of the mixture of contaminants within a specific toxicological category (e.g. irritants, carcinogen, neurotoxicant, etc.). For each toxicological category, the toxicity index (T) is calculated by summing the ratios of the measured concentrations to the appropriate SMAC. For most compounds the 180-day SMAC was used; however, when a 180-d SMAC was not available, the 7-day SMAC was used. The air is considered acceptable if $T<1$ for each toxicological category. Details of the procedure are in JSC 20584. The calculation is identical to that given in the Russian official standard GOST P 50804-95, part 6.2.2.3 (validity date 1/7/96); however, the Russians use quite different values for maximum allowable concentrations.

2.5 List of Pre-, In-, and Postflight Anomalies

There were only 2 anomalies associated with the process of air analysis. One GSC (#1034) was returned from the flight without being used to sample air (still under vacuum). The special target analysis for Freon 82 and Freon 218 was not completed on GSC #1020 due to malfunction of the inlet system to the GC/MS.

3. Results

The detailed analytical results found by GC and GC/MS are presented in tables 1 to 4, and the T values for individual contaminants are presented in tables 5 to 8. The results are given in the following order: canister samples, first SSAS (#0013), second SSAS (#0011), and Russian AK-1 sampler. Sulfur hexafluoride was found in all GSCs, but was not quantified because the compound is nontoxic and standards were not readily available. In table 9 the formaldehyde results have been summarized from the spectrophotometric analysis of the badges exposed on orbit. The T values for each important toxicological category are presented in table 10 for the canister data. T-value data from the SSAS (tables 6 and 7) indicated that the compounds did not need separation into toxicological categories in order to determine that the T values by category were below 1. The purpose of the AK-1 sample was to determine how closely it matched results from the other samples taken at the same time, so a T-value analysis by toxicological category was not performed.

Quality assurance and control is an essential part of sample acquisition and analysis. Three surrogate compounds were added before flight to each GSC and to each tube in the SSASs, and the SSAS flow rates were checked before and after flight. The surrogate compounds were selected to be representative of various classes of compounds found in most air samples. The surrogate recoveries and flow-rate changes were as follows:

Sampler Group	acetone-C13	fluorobenzene-D5	chlorobenzene-D5	flow differences (+/- from mean)
Mir-GSCs	85 to 110 %	88 to 111 %	90 to 104 %	not applicable
Mir-SSAS-0013	34 to 54 %	88 to 96 %	82 to 95 %	3.6 to 11 %
Mir-SSAS-0011	52 to 65 %	95 to 106 %	93 to 108 %	4.1 to 15 %

The SSAS tubes include only those tubes that were used during the flight to sample air. Except for the recoveries of acetone-C13 from the SSASs, all recoveries and flow differences were within acceptance ranges. This does not include tubes that were not used for sampling.

Another quality assurance procedure was pressure tracking of each canister to detect any leaks. Typically, the pressure was reduced from about 14.5 psia to about 6.5 psia as aliquots were removed from the GSCs for analysis by GC and GC/MS. Before the GC/MS was used for sample analysis, it had to pass daily calibration checks for 66 compounds and ion abundance criteria for bromofluorobenzene. Positive and negative controls were flown with the formaldehyde badges or kept in the laboratory to determine recoveries from samples with known dosing and suitably-delayed analysis. The recoveries from the 3 positive-control badges were 90 to 96 %.

4. Discussion

The most important hypothesis was that the air in Mir would pass U.S. standards for spacecraft air quality for a long mission. The data in table 10 suggest that this hypothesis has been confirmed with the minor caveat that the T value for carbon dioxide averaged slightly above 1 during the 3-month mission.

The second hypothesis we hoped to test was the air-mixing time after hatch opening between the Shuttle and the Mir. The sample taken at 0754 on 1/15/97 was slightly before hatch opening and the samples at 0936 and 1140 were approximately 1 and 3 hours after hatch opening, respectively. Many of the compounds show comparable concentrations in the two samples; however, several compounds exhibit distinct trends. The trends indicate the movement of Shuttle pollutants into the Mir (values increasing), or they indicate dilution of the Mir pollutants by Shuttle air that has lower concentrations of the pollutant (decreasing concentrations). Compounds that show a clear increase in Mir were ethanol, isopropanol, and bromotrifluoromethane (halon). The cause of the ethanol increase is uncertain; however, isopropanol levels are commonly much higher in the Shuttle than on Mir. Bromotrifluoromethane is the Shuttle fire extinguishant, and it seems that small concentrations of this nearly harmless gas reached the Mir Base block within a few hours. Compounds showing decreases in concentration in Mir were carbon monoxide, methane, and hydrogen. The proportional decreases (due to dilution) were not as large as the increases of the alcohols and halon because the Shuttle volume is much smaller than the volume of the Mir complex. In terms of the hypothesis, one additional sample (after the 3-hour sample) will be required to determine if the pollutants being exchanged between the Shuttle and Mir have reached a steady state condition. Changes were occurring between 1 and 3 hours after the hatch was opened.

The third hypothesis was that the variations in concentrations within the Mir complex will be small (<25%). Based on the canister data in table 1, this condition was met by the vast majority of compounds; however, the data from the base block seemed to differ from the concentrations found in the other 4 locations. It is not clear whether this is a true difference or an analytical anomaly; however, the excellent recoveries of surrogate compounds from this sample (acetone-87%, fluorobenzene-91%, and chlorobenzene-92%) indicate that there is a real difference. Since most of the increased compounds are solvents, one can speculate that a solvent or pen with volatile ink may have been in use at the time.

The last hypothesis concerned the consistency of results from the three primary methods of sampling. To assess this hypothesis we compared results from samples taken at about the same time in the same location. Specifically, we compared AK-1, GSC, and SSAS results from 11/11/96. The results of this analysis are given in table 11 for selected target compounds. The reader is reminded that the AK-1 and GSCs are instantaneous samplers (<5 minutes to sample), whereas the SSAS draws its sample over periods of approximately 24 hours. When ranges of data are compared in table 11, the GSCs and SSAS show good consistency; however, the AK-1 seems to give high results for

most compounds. To resolve the issue of differences in sampling by the methods it will be necessary to sample known atmospheres generated in the laboratory.

5. Conclusion

The Mir complex continues to exhibit air quality which substantially meets U.S. standards for human-rated spacecraft. The spatial variations seem to be limited to only a few compounds when the atmosphere is in a steady-state condition. The time for atmosphere stabilization after hatch opening could not be determined because too few samples were taken. The three basic sampling methods did not yield comparable measurements for some compounds.

6. Bibliography

1) Protocol for the Meeting of U.S. and Russian Experts on Mir Air Quality, Houston, TX, October 30 to November 6, 1995

2) Protocol of the Second Meeting of the Environments Subgroup of Medical Working Group 8, Houston, TX, October 21 to November 1, 1996

3) Perry, J.L. , J.T. James, H.E. Cole, T.F. Limero, S.W. Beck. Rationale and Methods for Archival Sampling and Analysis of Atmospheric Trace Chemical Contaminants Onboard Mir and Recommendations for the International Space Station. NASA/MSFC White Paper, November 1996

4) James, J.T., T.F. Limero, S.W. Beck, L. Yang, M.P. Martin, M.L. Matney, P.A. Covington, J.F. Boyd. Toxicological Assessment of Air Contaminants During the Mir 19 Expedition. NASA/JSC/SD2. 1996

5) Alexander, R.G. Mir-18 Containment Bag Failure. Memorandum NS5-95-180, September 26, 1995

6) James, J.T., T.F. Limero, S.W. Beck, L. Yang, M.P. Martin, M.L. Matney, P.A. Covington, J.F. Boyd, and D.A.W. Lind. Toxicological Investigation of Mir Air During NASA 2. Memorandum SD2-97-511, March, 1997

7) James, J.T., T.F. Limero, S.W. Beck, L. Yang, M.P. Martin, M.L. Matney, P.A. Covington, J.F. Boyd. Toxicological Assessment of Air Contaminants During the Mir 18 Expedition. NASA/JSC/SD2. 1995

Table 10. Analyses of Contaminants in GSCs by Toxicological Category

Category	Compound(s)	10/16/96 (1)[a]	11/11/96 (5)	12/10/96 (1)	1/3/97 (1)	1/15/97 (3)	3-Month Average
Irritants	formaldehyde	(0.50)[a]	(0.37)	(0.50)	(0.37)	(0.37)	
	acetaldehyde	0.03	0.03	0.02	0.02	0.03	
	propenal	1.14	0	0.33	0	0	
	3-butene-2-one	0.06	0	0	0	0	
	dimethyldisulfide	0	0.12	0.12	0.12	0.12	
	Total	1.73	0.52	0.97	0.51	0.52	0.85
Neurotoxicants	methanol	0.02	0.01	0.01	0.01	0.01	
	acetone	0.01	0.01	0.01	0.01	0.00	
	carbon monoxide	0.48	0.23	0.49	0.57	0.50	
	Total	0.51	0.25	0.51	0.59	0.51	0.47
Respiratory System Injury	OMCTS	0.06	0.07	0.06	0.10	0.09	
	HMCTS	0.08	0.16	0.12	0.20	0.18	
	DMCPS	0.20	0.15	0.07	0.21	0.13	
	Total	0.34	0.38	0.25	0.51	0.40	0.38
Carcinogens	furan	0.23	0.23	0.23	0.23	0.23	
	1,2-dichloroethane	0.02	0.02	0.02	0.02	0.02	
	Total	0.25	0.25	0.25	0.25	0.25	0.25
Gonad Injury	OMCTS	0.06	0.07	0.06	0.10	0.09	
	DMCPS	0.20	0.15	0.07	0.21	0.13	
	Total	0.26	0.22	0.13	0.31	0.22	0.23
“Explosives”	methane	0.17	0.19	0.22	0.22	0.19	
	hydrogen	0.03	0.03	0.02	0.03	0.03	
	Total	0.20	0.22	0.24	0.25	0.22	0.23
Cardiotoxicant	carbon monoxide	0.48	0.23	0.49	0.57	0.50	
	Freon 82	0.01	0.03	0.02	0.05	0.03	
	Total	0.49	0.26	0.51	0.62	0.53	0.48
Respiratory Physiology	carbon dioxide	0.93	1.01	0.92	1.08	1.12	1.01
Hepatotoxicity	dichloromethane	0.02	0.01	0.01	0.01	0.01	0.01

[a] Number of air samples available for averaging on the date above (except formaldehyde)

[b] Values in parenthesis are more than 3 days from the date in the column, but were the closest available. Area and personal samples were averaged for a given date.

Table 11. Similarity of Results from the Three Sampling Methods

Compound	Range of GSC Values[a] (mg/m3)	Range of SSAS Values[a] (mg/m3)	AK-1 Values[b] (mg/m3)
acetaldehyde	0.09 to 0.16	trace to 0.06	2.2
methanol	0.09 to 0.14	trace	0.42
ethanol	0.32 to 0.49	0.33 to 0.52	1.6
acetone	0.26 to 0.29	0.20 to 0.24	2.0
isopropanol	0.07 to 0.09	0.09 to 0.10	0.62
freon 11	0.23 to 0.27	1.3 to 1.4	1.2
dichloromethane	0.11 to 0.14	0.12	1.0
ethyl acetate	trace	trace	0.31
n-butanol	0.12 to 0.25	0.13 to 0.17	2.3
toluene	0.14 to 0.19	0.14	0.93
xylenes (o,m,p)	0.30 to 0.39	0.27 to 0.28	1.6
freon 82	11 to 13	0.8 to 0.9	1.3

[a] Range of values in samples from 11/11/96 5 different modules
[b] Values found in samples from 11/11/97 taken in base block and Priroda