TOXICOLOGICAL INVESTIGATION OF MIR AIR DURING NASA 5
(May 1997 to September 1997)

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February 1998

TOXICOLOGICAL ASSESSMENT OF MIR AIR DURING NASA 5

1. Introduction

Crew members aboard spacecraft are continuously exposed 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.

Early in NASA 5 (June 25, 1997), the Spektr module was severely damaged in a collision with a Progress module; it was sealed and depressurized. As a result, all formaldehyde badges, canister samplers, and SSAS devices for NASA 5 were lost for further use aboard Mir. In preparation for possible contingencies involving another fire or further leaks of ethylene glycol, detector tubes and a combustion products analyzer (CPA) had been placed aboard Mir. The importance of the ethylene glycol tubes became apparent after a large coolant leak that occurred on June 5, 1997 in the Kvant module.

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 large leak (>1 liter) of ethylene glycol will be scrubbed from the Mir atmosphere in 3 days. The opportunity to test this hypothesis depended on the availability of ethylene glycol detectors tubes and the occurrence of a leak of the appropriate size.

1.2 Objectives of the Experiment

Our primary objective was to periodically sample Mir air at various locations in the complex to assess the effect of airborne pollutants on crew health. Air samples were to be 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 Mir complex.

An additional objective emerged during the flight when the coolant loop in the Kvant module leaked a large quantity of ethylene glycol into the atmosphere. Since detector tubes were available to the crew, estimates of the concentrations could be made over a period of time and in modules at various distances from the site of the leak.

1.3 Background and History of the Project

The goal of our 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; however, concerns about ethylene glycol leaks had prompted us to fly detector tubes for this compound. These tubes were prepared and tested on a "crash" basis before they were taken to Mir.

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 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 recording of time and sample location. After flight, the samplers are returned to the NASA-JSC Toxicology Laboratory for analysis according to ISO 9000 laboratory work instructions . 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

Twelve 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 gas chromatography/mass spectrometry (GC/MS) for each target compound, 3) evacuation to $<10^{-5}$ torr, 4) addition of 10 ml of a gas-phase surrogate standard containing acetone-13C, chlorobenzene-D5, and fluorobenzene-D5, and 5) labeling of samplers for use in flight.

The solid sorbent air sampler (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.

At the request of the Phase I Program Office, the Medical Sciences Division was asked to determine the best-available technology for assessment of Mir atmosphere following a fire or ethylene glycol leak. Our response was to provide detector tubes for carbon monoxide and ethylene glycol, and to provide a CPA, which has been used on the Shuttle for years. The preflight preparation of the detector tubes included placing the tubes in a teflon sleeve to control broken glass, breaking the ends, and resealing the tubes with flexible caps.

Preflight testing of the detector tubes consisted of assessing the degree of interference from non-target compounds, the ability of the tubes to provide accurate measurements of the target compound, and the stability after the glass ends were broken and resealed. The results of this evaluation are given in table 1. The CO tubes were accurate and free of interference. The ethylene glycol tubes responded to acetaldehyde

in mixture 2, but the response could be distinguished from ethylene glycol. Acetaldehyde levels expected on Mir were well below those that would interfere with the measurement (table 2). The shelf lives of the tubes were determined by retaining some of the modified tubes as ground controls for periodic ground-based testing. The end caps on the CO tubes degraded after several weeks, and the Mir crew was told that these could not be used for measurements. The ethylene glycol tubes were tested for more than 4 months after repackaging for flight. Using a test concentration of about 18 mg/m3, fresh tubes gave average readings of 20 mg/m3 (range 18 to 20 mg/m3), whereas the repackaged, ground-control tubes gave an average of 16 mg/m3 (range 14 to 18 mg/m3). The repackaged ethylene glycol tubes were considered acceptable for use on Mir.

Preparation of the CPA included the usual functional checkouts performed for the Shuttle unit and preparation of a cable so that the unit could be recharged using Mir power. The CO, HCN, and HCl sensors were zeroed using clean air and the CO sensor was calibrated to read 50 ppm against a 50 ppm standard.

2.2 In flight Sampling of the Atmosphere

Due to the damaged Spektr module and the loss of all sampling devices inside, the only measurements obtained were from ethylene glycol detector tubes and the CPA. Ground-based testing of the carbon monoxide tubes showed that the end caps began decomposing within several weeks and that the tubes did not give reliable measurements. The ethylene glycol measurements were made as follows. Sealed packages were opened, end caps were removed from the pre-tube and indicating tube, and the reagent ampoule was broken by bending the pre-tube at a 45 degree angle. The tubes were connected with a rubber sleeve and the indicating tube was inserted into the hand pump. The pump was given 10 strokes and the length of the pink stain was read from the indicating tube, which has a scale from 10 to 180 mg/m3.

Measurements using the CPA were made at approximately 3-day intervals. The instrument was turned on, allowed to stabilize for 2 minutes, and readings of the CO, HCN, and HCl sensors were recorded in the log book. Often the readings were also given in the daily mission reports, which are the only source of our data since the mission log has not been returned.

In addition to the trace contaminant monitoring described above, the concentration of carbon dioxide is monitored on a near-continuous basis by Russian sensors aboard the Mir. The data are reported to ground-based controllers who compile the data and distribute it to appropriate users.

2.3 Post-flight Analyses of the Samples

No samples were available for post-flight analysis. The postflight checkout of the CPA showed that the instrument changed little during the long flight. The CO sensor read 0-1 ppm when exposed to fresh air and 50 ppm when exposed to the 50 ppm standard. The HCl sensor response was 0.0 ppm to clean air, and the HCN response was 0.1 ppm to clean air.

2.4 Toxicological Analyses of the Analytical Data

The estimates of ethylene glycol concentrations obtained during the mission were compared to spacecraft maximum allowable concentrations for this compound for the times of crew exposure. Because additional data were not available because of the Spektr loss, the assessment was considered incomplete at best.

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

As indicated above, all archival sampling capability was lost as a result of the isolation of the Spektr module after its depressurization.

3. Results

A summary of ethylene glycol estimates is given in table 3. Although guidance was given by the Environments Subgroup of Medical Working Group 8, the location and time of each sample was mostly at the discretion of the crew. The measurements were spaced far apart in order to conserve the remaining tubes in the event of another leak from a coolant loop.

The CPA readings were nominal except during the last days of the flight. From mission day 9 through 105 the sensors gave readings in the following ranges: CO, 0-3 ppm; HCN, 0.0 to 0.4 ppm; and HCl , 0.0 to 0.2 ppm. The HCN and HCl sensors remained in these ranges until the end of the mission; however, on mission day 106 the CO sensor gave readings of 11 and 7 ppm, and on mission day 128 the CO reading was 18 ppm. The cause of these high readings is unknown at this time. Much higher CO readings were obtained during NASA 6 with a different instrument. Since canister samples were taken at the same time, the analysis of those samples may reveal the cause of the high readings.

The maximum and minimum concentrations from monitoring of carbon dioxide are shown in the figure. The concentrations averaged about 4.8 mmHg with a variability range of approximately 4 mmHg.

4. Discussion

The loss of sampling capability makes it impossible to assess the general air quality aboard Mir. Based on earlier results, it is reasonable to expect that the atmosphere met U.S. standards for human-rated spacecraft. The ethylene glycol estimates did give us a chance to test the hypothesis that such leaks only pollute the air for a few days after they occur. This hypothesis was founded on the concept that the high water solubility of ethylene glycol and its relatively low volatility would make it easily removed from air by the humidity control system. Based on the data in table 3, that hypothesis must be considered incomplete at best.

The data in table 3 show that ethylene glycol was not evenly distributed inside Mir after the leak. The core module, which is adjacent to Kvant, showed consistently lower readings than the Kvant module where the leak occurred. The long term (7-180 day) SMAC for ethylene glycol is 13 mg/m3. The airborne concentrations in the Kvant module were well above this limit for the first month after the leak; however, the crew spent most of their time in other locations in the station. The concentrations in the core module dropped from 15 mg/m3 just after the leak to 10 mg/m3 within 6 days of the leak. This is essentially at the SMAC level for 7 days of exposure. Where comparisons can be made, levels in the more distal modules (Krystall and Spektr) were much lower than in the core module or Kvant. Ethylene glycol is not evenly distributed within Mir nor is it scrubbed from the atmosphere within a few days.

The behavior of ethylene glycol in Mir can be explained by postulating that when it is released into the air it condenses on cold surfaces near the location of the leak. Since its volatility is low, the pollutant evaporates very slowly back into the air where some is removed in the humidity condensate. Even though ethylene glycol vapor near the humidity condensing system will be removed, it can also recondense on other cold surfaces a little further from the original leak. Thus ethylene glycol does not spread quickly throughout the spacecraft nor is it easily removed. This postulate is supported by reports from the crew that large amounts of liquid condensate are present behind panels on Mir.

The carbon dioxide concentrations averaged 4.8 mmHg which is below the U.S. SMAC for long-term exposure of 5.3 mmHg. The SMAC was set at this level to minimize the risk of hyperventilation in crew members.

5. Conclusions

Loss of samples precluded a toxicological assessment of the atmosphere; however, we had the opportunity to observe the dynamics of ethylene glycol concentrations, which proved to be different than expected. Measurements after a large leak of ethylene glycol showed that this pollutant does not distribute evenly in the Mir complex like most airborne pollutants. It is difficult to remove from the atmosphere except near the point where water vapor is being condensed to control humidity, apparently because condensate reservoirs of ethylene glycol form on cold surfaces in the vicinity of the leak.

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 Technical Memorandum 108534, April 1997

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 1. RESULTS OF TESTING DETECTOR TUBES FOR SELECTIVITY: STS-84

Component		Concentrations Present										
		Blank	Accuracy Test			Test Gases for the Cross Sensitivity Studies						
carbon monoxide (ppm)		0	0	10	50	10	0	10	0	0	0	0
ethylene glycol (mg/m3)		0	18	0	0	0	18	0	18	0	0	0
mixture 1 (see table 2)		no	no	no	no	yes	yes	no	no	no	no	no
mixture 2 (see table 2)		no	no	no	no	no	no	yes	yes	no	no	no
octafluoropropane (ppm)		no	no	no	no	12	12	no	no	no	no	no
freon 82 (ppm)		no	no	no	no	5	5	no	no	no	no	no
carbon dioxide (mmHg)		no	no	no	no	7.6	7.6	no	no	no	no	no
hydrogen (ppm)		no	no	no	no	no	no	no	no	200	no	no
methane (ppm)		no	no	no	no	no	no	no	no	no	1000	2000
detector responses	**CO**	**0**	**0**	**10**	**50[c]**	**10**	**<1**	**10**	**<1**	**<1**	**<2**	**<1**
	EG	**0**	**20[c]**	**0**	**0**	**<5**	**20**	**<5[a]**	**20-50[b]**	**--**	**--**	**--**

[a] A yellow stain extending to about 15 mg/m^3 was present, but could be easily distinguished from the pink stain of ethylene glycol

[b] Stain was distinct up to 20 mg/m^3, but was irregular and more yellow (peach colored) between 20 and 50 mg/m^3.

[C] From vacuum-packaged bags as configured for flight

TABLE 2. Test Mixtures

MIXTURE 1

Compound	Max Conc NASA 2[a]	Test Conc.
Acetone	0.9[b]	9.5
Ethanol	5.4	15
isopropanol	1.1	9.8
butanol	0.6	1.2
2-butanone	0.08	1.2
Dichloromethane	0.24	5.5
1,1,1-Trichloroethane	trace	2.2
toluene	0.43	1.5
xylene	0.77	1.7
Freon 113	trace	4.6
Halon 1301	0.27	1.2

MIXTURE 2

Compound	Max Conc NASA 2	Test Conc
Chloromethane	0.2	2.1
Methanol	0.43	0.5
Acetaldehyde	0.24	1.1
2-butanone	0.08	2.1
isopropanol	1.1	1.7
freon 12	15	4.9
Toluene	0.43	3.8

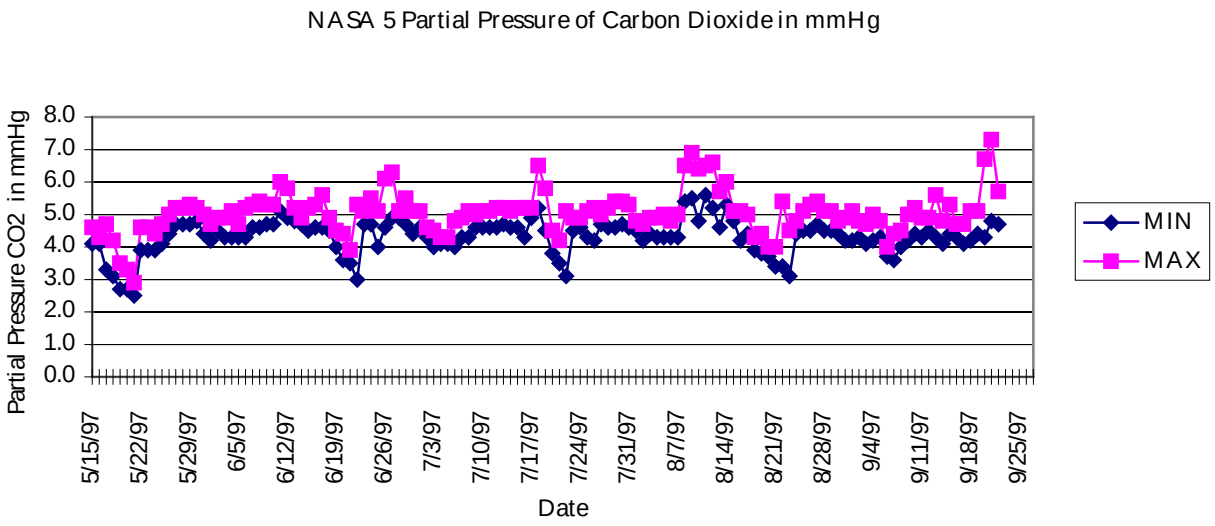
Other Compounds Not Evaluated Due to Low Levels in Mir

Styrene	trace
vinyl acetate	not detected
formaldehyde	0.12

[a] Maximum concentration detected in U.S. grab samples or solid sorbent sampler.
[b] Concentrations are shown in mg/m3

TABLE 3. Estimated Concentrations (mg/m3) of ethylene glycol following the leak in Kvant on 6/5/97.

Date (1997)	Kvant Module	Core	Krystall	Specktr	Soyuz	Transfer Module
6/5	75	15	0	--	--	--
6/6	30	15	3	3	--	--
6/8	30	15	--	--	--	--
6/11	20	10	--	--	--	--
6/16	18	3	--	--	--	--
6/23	18/20	10	--	--	--	--
7/1	15	3	--	--	--	--
7/24	<10	<3	--	--	--	--
8/4	--	<3	--	--	<3	--
8/8	15	--	--	--	--	--
8/23	12	--	--	--	--	<3
9/1	<3	--	--	--	--	--


NASA 5 Partial Pressure of Carbon Dioxide in mmHg
Partial Pressure CO2 in mmHg
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
5/15/97
5/22/97
5/29/97
6/5/97
6/12/97
6/19/97
6/26/97
7/3/97
7/10/97
7/17/97
7/24/97
7/31/97
8/7/97
8/14/97
8/21/97
8/28/97
9/4/97
9/11/97
9/18/97
9/25/97
Date
MIN
MAX