180-DAY PRELIMINARY SCIENCE REPORT

Performed under
NASA contract NAS 9-19410
"Analysis of Volatile Organic Compounds on Mir Station"

Submitted By:
Peter T. Palmer, Ph.D., Principal Investigator
Department of Chemistry & Biochemistry
San Francisco State University
San Francisco, CA 94132-1722
Phone: (415) 338-7717
Email: palmerp@lewis.sfsu.edu

Warren Belisle, Co-Investigator
Analytical Chemistry Laboratory
Lockheed-Martin Technical Services
NASA Ames Research Center, MS 239-11
Moffett Field, CA 94035-1000
Phone: (415) 604-5252
Email: wbelisle@mail.arc.nasa.gov

Submitted To:
NASA Johnson Space Center
2101 NASA Road 1
Houston, TX 77058-3696

Submission Date:
July 22, 1997

I. INTRODUCTION

The goal of this research is the characterization of volatile organic compounds (VOCs) in air samples from Mir Space Station using new technology based on ion trap mass spectrometry (ITMS). Twenty-four hour time-averaged samples will be collected onto cartridges using the US Solid Sorbent Air Samples (SSAS). Grab samples will be collected using US Grab Sample Containers (GSC). Samples will be transferred from Mir via the Space Shuttle, forwarded to the Toxicology Laboratory at NASA Johnson Space Center (JSC) for analysis and sample subdivision, and then sent on to San Francisco State University (SFSU) for the purposes of this work. Standard operating procedures, quality control samples, and confirmatory experiments will be employed to ensure reliable, high quality data. Analyses will be performed via a modified form of EPA-approved gas chromatography/mass spectrometry (GC/MS) methods [1] and new techniques based on direct sampling ion trap mass spectrometry (DSITMS). Significant effort will be put into developing, testing, and demonstrating DSITMS techniques with the requisite sensitivity, selectivity, and speed for real-time monitoring of trace-level contaminants in air. The results of this research will provide detailed information on the types and concentrations of VOCs in the Mir environment. Moreover, the demonstration of new technology and comparison against proven methods will yield valuable information on the feasibility of its use for monitoring air quality in advanced life support systems.

A. Hypotheses

1. The types and concentrations of VOCs in the Mir Station atmosphere are not well characterized. Detailed information on the types and concentrations of VOCs in the Mir Station atmosphere is required to assess the toxicological risks of long-term human exposure to this environment.
2. Detailed information on the types and concentrations of VOCs in the Mir Station atmosphere can be obtained through the use of the same proven methods employed for previous US space missions. These methods, based on the use of both cartridges and grab samples for sampling, and GC/MS for analysis, represent the most reliable, cost-effective means for characterizing this environment.
3. New technology based on DSITMS shows excellent promise for on-line, real-time monitoring of VOCs. Demonstration of this technology on air samples collected from Mir Station can provide a means for intercomparison with conventional GC/MS methods and provide a measure of its potential for environmental health assessments and advanced life support applications.

B. Objectives of Investigation

1. Characterize Mir Station atmosphere via proven sampling and analysis strategies.
2. Demonstrate the use of DSITMS for direct monitoring of VOCs in air samples collected from Mir Station.
3. Document the types and concentrations of VOCs on Mir Station and analyze results in collaboration with other science investigators to further the goals of the NASA Research Announcement (NRA).

C. Background / History of Project

Palmer and the JSC Toxicology Lab have signed a Memorandum or Understanding (MOU) that details the nature of their collaborative research on characterization of VOCs in Mir air samples. The JSC Toxicology Lab has extensive experience on space station air analysis and flown SSAS and GSC units on a variety of prior NASA missions ranging from the Apollo through the Shuttle programs [2-6]. Palmer and Belisle have additional experience analyzing for VOCs in air samples collected in various locations in the San Francisco Bay Area [7], boreal ecosystems [8], and bioregenerative life support chambers [9,10].

Palmer's mission experience includes a set of "practice" samples from the Mir 19 mission. These samples enabled the testing of analytical methods and instrumentation, and the garnering of practical experience on space station air samples. Analytical results on these samples, that is compounds tentatively identified and their concentrations, were reviewed with researchers at the JSC Toxicology Lab [11]. These

results generally showed good agreement with those from the JSC Toxicology Lab. A final report on the analysis of air samples from the Mir 19 mission was recently submitted [12].

Palmer's mission experience also includes a set of samples from the Mir 21 mission. The Mir 21 samples were analyzed as per the objectives as stated here. A 180-day report on these samples was recently submitted to JSC Toxicology Lab [13]. These results will be reviewed and a final report submitted in October 1997.

II. METHODS/RESEARCH OPERATIONS

A. List and Description of All Functional Objectives

FO1. Collect instantaneous air samples using GSCs
FO2. Collect 24-hour time-averaged samples using the SSAS unit

B. List and Description of All Hardware Items Used

HW1. GSC - Grab sample container capable of collecting an instantaneous air sample
HW2. SSAS - Solid Sorbent Air Sampler capable of collecting up to 7 time-averaged air samples

C. Sessions Table

Table 1. Sessions/functional objectives table

mission	session name	FO#	scheduled HW#	scheduled day	actual day	scheduled subjects	actual subjects	samples/ parameters	method
Mir 22	collect GSC sample AA01336	*	FO1	HW1	N/A	4-Apr-96		-	-
Mir 22	collect GSC sample AA01339	*	FO1	HW1	N/A	18-Jun-96		-	-
Mir 22	collect SSAS sample *		FO2	HW2	N/A	N/A	-	-	AA01353
Mir 22	collect SSAS sample *		FO2	HW2	N/A	N/A	-	-	** tube #4

Notes:
N/A refers to the fact that this information was not available at this time
* denotes that information on the methods is provided below in section D
** denotes that no sample ID was provided by the JSC Toxicology Lab for this sample, henceforth in this document, it will be referred to as SSAS tube #4

D. Discussion of Method/Protocol

Specific methods to delineate the steps involved with unstowing the sampling devices, collecting air samples, restowing the sampling devices, and transferring the sampling devices to and from the Shuttle have been documented by the JSC Toxicology Lab. The methods used to collect air samples using these devices are briefly described here. For GSCs, this involves recording the date, time, and location; opening a valve on the GSC to begin collection of the air sample; and then closing the valve once the GSC pressure has reached ambient pressure. For the SSAS unit, this involves recording the date, time, and location, switching the valve on the SSAS unit from a "park" location to one of the 7 sampling tube locations, and turning on the sampling pump to begin collection. After the desired sampling interval is complete (usually ~24 hours), the date and time are again recorded, the sampling pump turned off, and the valve is switched back to the "park" location.

III. RESULTS

A. List of Pre-, In-, and Post-Flight Anomalies

The valve on the GSC corresponding to sample AA01336 was found to have been left in the open position upon receipt from the JSC Toxicology Lab.

B. Completeness/Quality of Data

A number of GSC and SSAS samples were collected on the Mir 22 mission and returned to the JSC Toxicology Lab for analysis. A subset of these samples that included 2 GSC and 2 SSAS samples (samples AA01336, AA01339, AA01353, and Tube #4) were forwarded to Palmer and Belisle in February. As described above, one of these samples (AA01336) was compromised and hence not analyzed.

C. Tables, Graphs, Figures Index

Table 1. Sessions/functional objectives table
Table 2. Mir 22 sample information
Table 3. Results from the analysis of sample AA01339
Table 4. Results from the analysis of sample AA01353
Table 5. Results from the analysis of sample Tube #4
Table 6. Summary of VOCs identified in Mir 22 samples

IV. DISCUSSION

A. Status of Data Analysis

Analysis of the samples using a modified form of standard EPA GC/MS methods [1] was successful. Preliminary results of the data analysis on these samples are provided in this report. These results will be discussed with colleagues at the JSC Toxicology Lab to provide critical review and intercomparison .

Analysis of samples via DSITMS methods have been put on hold to permit further development of this new technology, preparation of appropriate gas standards, and generation of the analytical methods needed to monitor specific target VOCs in the samples. It should be noted that there are currently two critical limitations to the successful application of DSITMS techniques to the analysis of VOCs in Mir air samples: sample volumes and detection limits.

DSITMS analyses based on the use of a current sample introduction system requires volumes on the order of 0.1 to 1 L. The actual volume of Mir air samples are approximately 1 L, and this volume is further reduced by prior GC/MS analyses by both the JSC Toxicology Lab and Belisle. Although the samples can be repressurized to provide a larger volume for DSITMS analysis, this dilutes the VOCs to lower concentrations.

The current detection limits of DSITMS techniques are approximately 50 part-per-billion by volume (ppbv) [14]. GC/MS data on the Mir 22 samples showed as few as 3 and as many as 8 VOCs whose concentrations exceeded this 50 ppbv level out of the 66 target compounds. Despite the somewhat limited scope of DSITMS relative to the GC/MS, this technique will be used to analyze for all VOCs in the Mir 22 samples whose concentrations were found to exceed 50 ppbv via GC/MS analyses.

It should be noted that air quality monitoring in a space environment requires an analytical technique that has a detection limit at least one order of magnitude lower than the space maximum allowable concentration (SMAC). Given that all but a few of the target VOCs have SMACs in the ppmv range [15,16], it is apparent that DSITMS techniques should be able to monitor most other VOCs at concentrations well below their SMACs.

B. Preliminary Research Findings

1. Introduction

Two types of samples were collected from Mir station: grab samples using GSCs and time-averaged samples using the SSAS unit. Information describing where and when these samples were collected and how they were processed was provided by the JSC Toxicology Lab and is shown in Table 2.

Table 2. Mir 22 sample information

JSC ID	GSC S/N	Sample Type	Sampling Location	Sampling Time	Notes
AA01336	13724	GSC	Krystal	22:00, 4-Apr-96	valve left open - sample lost
AA01339	13717	GSC	Spektr	11:30, 18-Jun-96	
AA01353	21499	SSAS tube #1	Spektr	N/A	
Tube #4	22526	SSAS tube #4	Spektr	N/A	

2. Experimental

Mir samples and standards were analyzed using a modified form of the EPA TO-14 method [1]. The most salient experimental details on analytical methods employed are summarized here. Detailed information on preparing standards, tuning the GC/MS instrument, and quality assurance/quality control (QA/QC) procedures are beyond the scope of this report and are documented elsewhere [17].

An Entech 7000 concentrator was used to isolate the VOCs from the bulk of the air sample. Samples were pulled out of a stainless steel canister and passed through a cryogenically cooled internal trap. VOCs were desorbed from this internal trap, passed through moisture control and carbon dioxide removal modules, and cryofocused onto the head of the GC column. Injection was achieved by flash heating the head of the column..

A Varian Saturn 3 gas chromatograph/ion trap mass spectrometer/data system was used to separate and detect individual VOCs. A 150 m, 0.23 mm ID Petrocol column was used to effect the separation. Identification of specific VOCs in the Mir samples was achieved via a combination of both a retention time match to a known standard and library searching of mass spectral data. Retention time information for each target VOC was obtained from the analysis of commercial and custom gas standards. Library searching was accomplished by matching experimental mass spectra against the NIST library of approximately 60,000 reference mass spectra. Identification and quantitation was performed using Varian EnviroPro software. The results were entered into a Microsoft Excel spreadsheet a and concentrations in the original Mir samples were computed using sample processing data provided by the JSC Toxicology Lab.

A number of QA/QC procedures were implemented for these analysis. A Supelco TO-14 100 per-billion by volume (ppbv) gas standard which contained 37 common VOCs was used to prepare a series of working standards. Neat stock solutions for 29 additional VOCs were made and used to prepare additional series of working standards. Canisters used to contain these working standards were cleaned with humidified, purified air and their cleanliness “proofed” by GC/MS analysis prior to use. Five point calibration curves were established for each VOC. Blanks were analyzed to ensure that the sample path through both the Entech unit and GC/MS instrument were not contaminated. Mass spectrometer response was tuned to meet EPA criteria for bromofluorobenzene. Internal standards were employed in standards and samples to correct for variations in instrument response. Replicate analyses employing volumes of 200 and 50 mL were performed on each Mir sample.

3. Results

Results from the analyses of samples AA01339, AA01353, and tube #4 are shown in Tables 3, 4, and 5. The “nd” in these tables refers to a VOC that was not detected. Concentrations in this report are given in units of ppbv which, unlike the conventional EPA units of mg/m3, are independent of temperature and pressure. There is a large amount of information in these tables and some discussion of their content is necessary to facilitate their interpretation. A summary of the VOCs identified in these samples, their possible sources, range of concentrations, and 7-day SMACs are given in Table 6.

The target compounds for these analyses included 37 VOCs in the TO-14 standard plus an additional 29 VOCs. This latter set of 29 VOCs encompassed fluorocarbons, siloxanes, terpenes, and oxygenated hydrocarbons which were either identified in samples from prior Mir missions and toxic and/or

potential contaminants. Out of the total of 66 target compounds, only 17 VOCs were identified at measurable concentrations in all 3 samples. Most of these are common air contaminants that can be categorized into specific compound classes shown in Table 6 and are not unexpected for the Mir environment. Although d5-chlorobenzene was also identified in the samples, this compound was added to the canisters prior to their use by the JSC Toxicology Lab as a surrogate standard and was not actually present in the Mir environment. The presence of siloxanes in the Mir samples may be somewhat questionable. Belisle found that relative responses of siloxane gas standards undergo a rapid decay over the first few days and eventually stabilize after a week. This behavior could be explained by these compounds occupying active sites on the canisters. Turning this argument around, one could hypothesize that high carbon dioxide and water content of the Mir samples may occupy active sites on the canisters and displace siloxanes that have been adsorbed onto their surface, causing their apparent concentration in the Mir samples to be higher than their true values. A NASA report suggest that these compounds may have a common system source and hence may not actually be present in the Mir samples [18]. Clearly, further work on the source and stability of siloxanes in canisters is warranted.

Quantitative results from replicate analyses of 200 and 50 mL sample volumes agree fairly well. Precisions ranged from 1 to 50% relative standard deviation (%RSD), compared to the nominal 25% precisions expected for these methods [18]. Notable exceptions to this include trichlorofluoromethane, trichlorotrifluoroethane, and methylene chloride. In the worst case, trichlorofluoromethane was not identified in the 200 mL run and identified in the subsequent 50 mL run at 1125 ppbv in sample AA01339. As these compounds are common chlorocarbons likely to be present at relatively high concentrations in any working lab, it is possible that their presence in the Mir samples may be caused by a systematic error related to their extreme volatility. Further work to identify the cause of this poor reproducibility is needed. The differences in VOC concentrations between the various samples is understandable given their different sampling locations, times, and methods (GSC vs. SSAS). Finally, it should be noted that VOC concentrations were several orders of magnitude below their SMACs, indicating the air samples were fairly clean.

Insert Table 3 here (separate Excel file)

Insert Table 4 here (separate Excel file)

Insert Table 5 here (separate Excel file)

Table 6. Summary of VOCs identified in Mir 22 samples

compound	possible source	concentration (ppbv)	SMAC (ppbv)
chlorinated hydrocarbons:			
trichlorofluoromethane (Freon 11)	refrigerant	nd-208	71,200
trichlorotrifluoroethane (Freon 113)	refrigerant	54-184	50,000
methylene chloride	solvent	nd-186	15,000
1,1,1-trichloroethane	solvent	nd-18	29,300
fluorinated hydrocarbons:			
perfluoro-1,3-dimethylcyclohexane	refrigerant/solvent	19-609	N/A
aromatic hydrocarbons:			
toluene	fuel	62-153	16,000
ethylbenzene	fuel	7-18	30,000
o-xylene	fuel	26-68	50,000
m-and p-xylene	fuel	15-26	50,000
terpenes:			
limonene	plant emission	52-237	N/A
oxygenated hydrocarbons:			
hexanal	human metabolite?	nd-17	N/A
2-butanone (MEK)	human metabolite?	nd-134	10,000
ethyl acetate	human metabolite?	nd-10	N/A
n-butyl acetate	human metabolite?	nd-25	52,700
2-ethyl-1-hexanol	human metabolite?	60-139	N/A
siloxanes:			
hexamethylcyclotrisiloxane	plastic offgas	78-208	25,300
octamethylcyclotetrasiloxane	plastic offgas	46-315	100,000

More detailed evaluation of these results will be presented in the 1-year report, which will include critical feedback from the JSC Toxicology Lab and a discussion on comparison of results.

C. Conclusions

The analyses of the Mir 22 samples showed common VOCs normally found in air samples. This included chlorinated hydrocarbons, fluorocarbons, aromatic hydrocarbons, terpenes, oxygenated hydrocarbons, and siloxanes. All of these VOCs were present at concentrations several orders of magnitude below their SMACs. In fact, these results show air quality on board Mir station to be better than most indoor environments, insofar that there were fewer VOCs detected and those that were found were present at relatively low concentrations. The investigators have a high degree of confidence in the results, due to past experience on samples from Mir 19 and 21 missions, implementation of a number of QA/QC procedures, and good agreement between replicate analyses. These results will be compared with those from the JSC Toxicology Lab and reviewed with their scientists.

Palmer and his students have made continuing progress in the development and application of DSITMS techniques for the real-time analysis of VOCs in air. Thus far, two different sample introduction systems have been studied, including both continuous and discrete inlets [14]. Studies into the optimization of experimental parameters for MS/MS scan functions were recently completed [19]. DSITMS methods have been developed and calibration curves have been established for 6 different compounds including trichlorofluoromethane (Freon 11), dichlorodifluoromethane (Freon 12), carbon tetrachloride, benzene, toluene, xylene, and a-pinene [20-22]. This research has made it possible to reliably apply these techniques

to the analysis of VOCs in Mir samples, and the analyses of Mir 22 samples via DSITMS techniques are currently in progress. Further research will address the development of a new two-stage membrane inlet capable of lower detection limits, continued development of DSITMS methods for target VOCs, and their application to Mir samples. This research will be documented in the 1-year report.

V. BIBLIOGRAPHY

Anonymous, Compendium Method TO-14: The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Summa Passivated Canister Sampling and Gas Chromatographic Analysis, US EPA, Research Triangle Park, NC, May 1988.

W.J. Rippstein, “The Role of Toxicology in the Apollo Space Program”, in R.S. Johnston, L.F. Dietlein, and C.A. Berry (Eds.), Biomedical Results of Apollo, NASA SP 368, NASA, Washington, DC, 1975.

H.M. Liebich, W. Bertsch, A. Zlatkis, and H.J. Schneider, “Volatile Organic Components in the Skylab 4 Spacecraft Atmosphere”, Aviation, Space, and Environmental Medicine, Aug. 1975, p. 1002.

J.T. James, T.F.Limero, H.J. Leano, J.F. Boyd, and P.A. Covington, “Volatile Organic Contaminants Found in the Habitable Environment of the Space Shuttle: STS-26 to STS-55”, Aviation and Space Environmental Medicine, 65, 1994, p. 1.

M.L. Matney, J.F. Boyd, P.A. Covington, H.J. Leano, D.L. Pierson, T.F.Liermo, and J.T. James, “Comprehensive Analysis of Airborne Contaminants from Recent Spacelab Missions”, 6th Annual Workshop on Space Operations, Applications, and Research, Vol. 2, Feb. 1993, p. 579.

T.F. Limero, “The Use of Mass Spectrometry Aboard United Spaces Spacecraft”, in D.L. Andrews and A.M. Davies (Eds.), Frontiers in Analytical Spectroscopy, Royal Society of Chemistry, Cambridge, UK, 1995.

L. Bogdanovic and P.T. Palmer, “Analysis of CFC Levels in Silicon Valley Air Samples”, Western Regional Meeting of the American Chemical Society, San Francisco, CA, Oct. 28 - Nov. 2, 1996.

M. Lerdau, M. Litvak, P. Palmer, and R. Monson, "Controls Over Monoterpene Emissions from Boreal Forest Conifers", Tree Physiology, manuscript in press.

P.T. Palmer and C.M. Wong, "Development of Ion Trap Mass Spectrometric Methods to Monitor Air Quality for Life Support Applications", SAE Transactions - Journal of Aerospace, vol. 102, 1993, pp. 1276-1291.

W. Belisle, unpublished results.

P.T. Palmer, “Preliminary Results from the Analysis of Air Samples from the Mir 19 Mission”, Sep. 1996.

P.T. Palmer, “Final Report on the Analysis of Air Samples from the Mir 19 Mission”, Apr. 1997.

P.T. Palmer, “NASA-2 / Mir 21 180-Day Preliminary Science Report”, Apr. 1997.

P.T. Palmer and D. Karr, “Evaluation of Two Different Direct Sampling Ion Trap Mass Spectrometry Methods for Monitoring Volatile Organic Compounds in Air”, Journal of the American Society for Mass Spectrometry, manuscript submitted.

JSC Toxicology Group, “Spacecraft Maximum Allowable Concentrations for Airborne Contaminants”, JSC 20584, Feb. 1995.

JSC Toxicology Group, “Spacecraft Maximum Allowable Concentrations”, May 1997.

W. Belisle, “Analytical Operating Procedure for Volatiles in Air”, NASA Ames Research Center, Jul. 1997.

J.L. Perry, J.T. James, H.E. Cole, T.F. Limero, and S.W. Beck, “Rationale and Methods for Archival Sampling and Analysis of Atmospheric Trace Chemical Contaminants On Board Mir and Recommendations for the International Space Station, NASA Technical Memorandum 108534, April 1997.

Xinghua Fan and P.T. Palmer, “Using MS/MS for Environmental Analysis - Practical Considerations”, Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, CA, June 1-5, 1997, in press.

C. Remigi, P.T. Palmer, and D. Karr, "Real-Time Monitoring of Chlorofluorocarbons in Air via Direct Sampling Ion Trap Mass Spectrometry ", Proceedings of the 44th ASMS Conference on Mass Spectrometry and Allied Topics, Portland, OR, May 12 - 17, 1996, p. 523.

K. Coffee, L. Lee, and P.T. Palmer, "Direct Sampling Ion Trap Mass Spectrometry for Real-Time Monitoring of Monoterpenes”, Western Regional Meeting of the American Chemical Society, San Francisco, CA, Oct. 1996.

C. Remigi and P.T. Palmer, “Analysis of Aromatic Hydrocarbons in Air via Direct Sampling Ion Trap Mass Spectrometry”, Proceedings of the 45th ASMS Conference on Mass Spectrometry and Allied Topics, Palm Springs, CA, June 1-5, 1997, in press.

ACKNOWLEDGMENTS

Palmer would like to thank Tom Limero, John Boyd, Lilly Yang, and Marilyn Matney of the JSC Toxicology Lab for providing the samples and many helpful discussions. Support for this work was provided by NASA contract NAS 9-19410.