

N90-24977**IDENTIFYING ATMOSPHERIC MONITORING NEEDS
FOR SPACE STATION FREEDOM****Final Report****NASA/ASEE Summer Faculty Fellowship Program--1989****Johnson Space Center**

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ABSTRACT

The atmospheric monitoring needs for Space Station Freedom were identified by examining from an industrial hygiene perspective: the experiences of past missions; ground based tests of proposed life support systems; the unique experimental and manufacturing facilities; the contaminant load model; metabolic production; and a fire. A target list of compounds to be monitored is presented and information is provided relative to the frequency of analysis, concentration ranges, and locations for monitoring probes.

INTRODUCTION

The Space Station Freedom is designed to operate for extended periods, up to 180 days, without resupply by utilizing a regenerative, nearly closed loop life support system. Under normal operating procedures, overboard disposal of wastes and venting of gases to space will not be allowed. All waste materials will be treated and recycled. Concentrated wastes will be stabilized and stored for ground disposal. The thirty year life of the station and the diversity of materials brought aboard for experimental or manufacturing purposes increases the likelihood of cabin contamination. Sources of contamination include: biological waste production, material off-gassing, process leakage, accidental containment breach, and accumulation due to poor removal efficiencies of the purification units.

An industrial hygiene approach was used to identify monitoring needs for Freedom. Included was a preliminary review of monitoring requirements for analogous ground based situations when breathing air is supplied, in confined spaces and on nuclear submarines. It was clear that continuous monitoring should be provided for components critical for life support, and that intermittent analysis be provided for all agents that may exceed the Space Maximum Allowable Concentration (SMAC). The minimum monitoring effort should include continuous monitoring for: nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), water (H_2O), hydrogen (H_2), methane (CH_4), hydrocarbons, refrigerants, and halons.¹

In this paper the monitoring needs are identified by examining: the experiences of past missions; ground based tests; the station configuration; the life support system; the metabolic load from an 8-man crew; the contaminant load model; and a fire scenario.

SPACE STATION

The Space Station Freedom will have four modules: the U.S. Laboratory (USL); the U.S. Habitation module (USHAB); the Japanese Experimental Module (JEM); and the European Space Agency (ESA) module, Columbus. The modules are connected by four resource nodes. An airlock and a logistics module are connected to the resource nodes.

Air Revitalization System

Each module will have an independent Air Revitalization System (ARS) with an Environmental Control Life Support System (ECLSS) and a Trace Contaminant Control System (TCCS). The U.S. modules will have four ARS units, two in each module. Each ARS is designed to support four crew members. One ARS at a time will operate in each module.

The ARS will provide ventilation to each module and node but not to the airlock. Intramodule circulation will approximate near perfect mixing with an intermodule air exchange of 140 cubic feet per minute (CFM).² The ventilation design is based: on heat transfer and humidity control to maintain crew comfort; and on O₂ supply and CO₂ removal based on metabolic requirements.³ The air exchange rate will be 1-2 years, achieved through air loss from leakage and airlock extra vehicular activity (EVA).

The technology base for the TCCS is good and system tests have worked as predicted. The TCCS will consist of fixed bed charcoal filters, high efficiency particulate filters, and a high temperature (680 °C) catalytic oxidizer (palladium/aluminum) with pre and post sorbent beds of lithium hydroxide (LiOH). There will be four units, two in each module. The air flow through each catalytic oxidizer is 2.5 CFM, or 5 CFM for the two U.S. modules.⁴ Assuming a station volume of 900 M³, this is only 0.22 air changes per day of what should be considered as fresh air. This flow rate is low as, the indoor air quality ventilation guideline for fresh air intake is 15 CFM per person.⁵ This guideline is intended to keep odors to an acceptable level to 80% of the visitors entering the space and it assumes that one third of the occupants are smoking at the rate of 2.2 cigarettes per hour. The TCCS will receive cabin air from the temperature and humidity control system. It must handle purge gases that will be routed to the TCCS for contaminant removal from the ARS, waste water recovery, urine processing, waste reduction, storage systems, and lab racks.

U.S. Modules

The U.S modules will provide facilities for on-orbit repair, health maintenance, and a number of material processing and biological experiments intended to lead to manufacturing in space.

A maintenance work station will allow on-orbit repair of defective or damaged hardware. Processes likely to be required are drilling, sawing, welding, soldering, and epoxy gluing. A work bench/contaminant control console is envisioned that will collect the particulate and gaseous emissions generated in the repair process near their source.⁶ The rack would be equipped with filters and the air recirculated with some venting to the TCCS. The work station would be a source of particulates, metal fumes, and gases not encountered on prior missions.

The health maintenance facility will provide critical care for one individual for 28 days and outpatient care for the crew complement for the mission duration. The equipment and supply list for this facility will be lengthy.⁷ It may be an additional source of trace contaminants, mainly sterilants.

The U.S. Laboratory will provide facilities for experiments and manufacturing.⁸ The candidate facilities, experimental processes, and materials are being baselined. These processes will generate biologicals, combustion and oxidation products, acid gases, metal and crystal fumes, and assorted lab wastes. Approximately 300 chemicals and mixtures have been identified for use in USL experiments. An evaluation should be made to determine the probability of these agents to approach harmful concentrations. Also, many of these materials are capable of adversely affecting the ECLSS subsystems by poisoning the catalyst or absorption beds, or they could appear in the humidity condensate, the potable water supply. These materials will have to be stored, transported to the point of use, and the waste products handled. The lab racks will be contained with at least a two failure tolerant design. That is, there will be three levels of containment by procedure or seal. Each rack will be equipped with some type of contaminant control equipment and vented to the TCCS. The lab racks should be equipped with monitors, specific for the process they contain to detect internal leaks. The chemical storage area should be monitored, and the cabin atmosphere must be routinely sampled to alert the crew of any leak.

MONITORING NEEDS

Past Experiences

Experiences of past missions and ground based systems tests have identified a number of health concerns that should be addressed in a monitoring plan for Space Station Freedom. Paramount is the flight and post flight health complaints of the crews: headache; irritation of the eyes and upper respiratory tract; and odor complaints, symptomatic of noxious air.⁹ Early missions had insufficient monitoring data for evaluation, which indicated a need for a more comprehensive monitoring system. Analyses of activated carbon and LiOH filters of the atmospheric revitalization systems, and the active sampling and analysis for air contaminants of later missions have identified over 250 contaminants in spacecraft air.¹⁰ Most were observed at trace levels, well below the SMAC. Others may have been present in sufficient concentrations to elicit symptoms among crew members, may accumulate to harmful levels during extended missions, or may have potential to poison the spacecraft's life support system.

Nitrogen tetroxide (N_2O_4), hydrazine, and monomethyl hydrazine are the main liquid propellants to be used on Freedom. Because of the quantities involved and the frequency of EVA, some internal contamination will occur. The airlock will likely serve as a decontamination station and will contain a propellant monitor or probe. If elevated propellant concentrations are detected in the airlock, then that atmosphere will be dumped to space to prevent contamination of the cabin atmosphere. The air

revitalization and trace contaminant control systems have not been designed to handle high pollutant loads. N_2O_4 decomposes to NO_2 , so elevated NO_2 concentrations can be expected. Some N_2O_4 contamination occurred on Apollo-Soyuz.⁹

Halon 1301 is no longer the primary fire suppressant baselined for Freedom, but it is still used on the Shuttle and baselined for Columbus. Halon was detected on spacelab mission SL-1 and on Shuttle missions STS-3, and STS-4. The trace contaminant control system (TCCS) will only handle modest quantities. Halon degradation products are toxic and will poison the catalytic oxidizer. If a halon release occurs it may be necessary to vent the cabin air to space and repressurize. Monitoring should therefore be required for Halon 1301 as long as it is aboard Columbus and the Shuttle.

Methane (CH_4) is a metabolic product that accumulates as each mission progresses. It will likely be the contaminant of greatest concentration. The Bosch CO_2 reduction system, a candidate for the air revitalization system (ARS), will produce large quantities of methane. A high temperature catalytic oxidizer will be required to keep CH_4 concentrations below 1 ppm.^{4,11} Continuous monitoring for methane is recommended.

CO , a product of incomplete combustion, may be released from metabolic processes, smoldering of carbon filters, or fire. The Bosch CO_2 reduction system produces CO and the potential for rapid accumulation exists, if not removed by the trace contaminant control system.^{4,11} There are more deaths from CO poisoning than any other chemical agent, therefore, continuous monitoring for CO is recommended.

Ammonia (NH_3) is used in the active thermal control system on the Shuttle and possibly Space Station. It is a metabolic product that will be released from urine processing, and it is also a degradation product of the solid amine resin proposed for the ARS.¹² If not removed NH_3 will exceed SMAC values within days. The condensing heat exchanger is relied upon for NH_3 removal but phosphoric acid impregnated charcoal filters can also remove it. An NH_3 monitor is recommended.

Hydrogen will be produced by electrolysis and used in CO_2 reduction by both the Bosch and the Sabatier processes.^{4,11,13} A pressure gradient will be used to minimize the likelihood of explosive mixtures from developing, if a leak occurs. H_2 accumulation is likely and continuous monitoring is recommended.

Toluene was detected on a number of missions. On Shuttle mission STS-2, toluene approached the SMAC value in one sample. Subsequent analyses indicated that for the sample, the additive toxicity hazard index for systemic poisons was exceeded by 1.22 times, with toluene the major constituent.⁹ Toluene is also a

contaminant which off-gases from the solid amine resin of the ARS.¹²

Trimethylamine is a principal breakdown product of the solid amine resin of the ARS. The trimethylamine concentration has exceeded safe limits in tests of the ARS.¹² Because of the numerous trace organics off-gassing from solid amine process a post sorbent bed such as phosphoric acid impregnated charcoal will be used.

Glutaraldehyde escaped containment on Spacelab mission SL-D1. Glutaraldehyde is a preservative and disinfectant with irritating properties. It may also be used in electrophoresis experiments on Space Station.

Silicon oil was released on mission 61A, wetting surfaces and making decontamination difficult. Silicon compounds are catalyst poisons and will occur on Space Station.

Freons have been detected on all Shuttle missions.¹⁴ The degradation products are corrosive, irritating, toxic, and catalyst poisons. Freon 12 will be on Freedom and continuous monitoring is recommended.

A computer model developed from Shuttle activated charcoal canister analysis for TCCS contaminant removal studies indicated that five contaminants may exceed SMAC values: propenal (acrolein), an irritant; benzene, a systemic poison and carcinogen; o-diethylphthalate, an irritant; propylfluorosilane, an irritant and catalyst poison; and 2-methylhexane, a central nervous system depressant.¹⁵ Benzene has also temporarily exceeded SMAC values during preflight off-gassing tests.¹⁴

Ethanal (acetaldehyde), ethanol, dichloromethane, and acetone have a high frequency of occurrence on shuttle missions and are likely to be present on Freedom.¹⁴

Oxidation products will be produced in the catalytic oxidizer. Post sorbent beds are necessary to prevent the release of oxidants and free radicals to the cabin air from the TCCS. Also, it has been hypothesized that secondary pollutants are important in cabin atmospheres. Trial simulations have indicated that spacecraft cabins may develop elevated NO₂ concentrations and O₃ concentrations exceeding SMAC values.¹⁶ Oxidation products, NO₂, O₃, and formaldehyde, were among the contaminants suspected of causing irritation on Shuttle flights, although particulates from biological sources were an undisputed cause of crew discomfort.¹⁷ Intermittent monitoring is recommended for these contaminants.

Contaminant Load Model

The Space Station trace contaminant load model is being used to design the ECLSS such that no substance will exceed the SMAC.¹⁸ In the model the generation rates in mg/day for 214 contaminants were estimated for the Space Station, consisting of two habitation modules, two laboratory modules and a logistics module. That configuration is slightly larger than the configuration presently baselined. The generation rates, the corresponding SMACs, and the Space Station volume (900 M³) were used to estimate the time required to reach $\frac{1}{2}$ SMAC, provided no removal mechanisms were operating. Those agents without a SMAC were assigned a conservative value of 0.1 mg/M³. The time in days is given by:

$$T_{\frac{1}{2}\text{SMAC}} = \frac{\text{SMAC (mg/M}^3\text{)} [\text{SS Volume (900 M}^3\text{)}] (0.5)}{\text{Generation rate (mg/day)}}$$

Contaminants not reaching $\frac{1}{2}$ SMAC within 365 days would be controlled by leakage alone, provided all contaminant sources were considered by the model. In such a case, monitoring would not be necessary. Any contaminant which would not reach $\frac{1}{2}$ SMAC within 90 days could be excluded from monitoring requirements (provided all contaminant sources were considered by the model), since the SMAC would not be reached for 180 days. Presumably, samples will be returned for exhaustive ground based analysis at least every 180 days, thus providing adequate time for identifying any etiological agent and remedial action.

From the trace contaminant load model analysis, 34 contaminants were identified and listed below as candidates for onboard monitoring:

methanol
isopropyl alcohol
isobutyl alcohol
n-butyl alcohol
cyclohexanol
n-butylaldehyde
hexanal
heptanal
m-xylene
indene
propylbenzene
p-cymene
ethyl cellosolve
butylacetate
furan
sylvan
ethylacetoxycetate

vinyl chloride
allyl chloride
chlorobenzene
isobutylene chloride
trichloroethylene
tetrachloroethylene
methyl ethyl ketone
methyl isobutyl ketone
cyclopentanone
methylheptanone
isobutyl ketone
acetonitrile
nitromethane
mercury
trimethylsilanol
p-dioxane
tetramethyl-1,2-epoxyethane

Although Freon 113 was identified as a major contaminant in the model, it is not baselined for use in Freedom and can be excluded from consideration in monitoring. This list can be further refined by determining SMACs for those compounds with conservative values of 0.1 mg/M^3 assigned and by considering the ECLSS removal efficiency for each agent.

The contaminant load model did not consider: contaminants from new systems and technologies; chemicals used for experimental and manufacturing purposes; cleansers; disinfectants; maintenance and repair activities; nor a full metabolic load from an 8-man crew.

The load model also only considers the independent action of each contaminant. An evaluation should consider additive toxicological effects, as more than one contaminant will likely be present. Remember, it is standard practice to assume additive effects, unless independent action is known. Since the ECLSS design is based on a contaminant load model using 7-day SMACs and considers only independent action, an evaluation by toxicological effects category is necessary.

Metabolic Load

The trace contaminant load model considered metabolic contaminants from the breath, sweat, and flatus of only one crew member. Off-gassing from urine and feces were not considered since the waste management system was assumed to contain and eliminate these metabolites as a source of atmospheric contamination. However, the analysis of Skylab 4 atmosphere shows 40 % of the volatiles to be of physiological origin. The major constituents were acetone, 2-butanone, 2-propanol, 4-methyl-2-pentanone, and 2-octanone.¹⁹ The Space Station cabin atmosphere will be subject to the metabolic wastes of 8 crew members, and the waste management system will be vented to the TCCS which must handle the load. Major metabolic products which must be removed by the ARS and the TCCS are CO , CO_2 , NH_3 , H_2S , CH_4 , organic acids, ketones, alcohols, and mercaptans.²⁰

Production rates of human metabolites²¹ from an 8-man crew were used to determine the time required for these contaminants to reach $\frac{1}{2}$ SMAC. The metabolic products and values are shown below. Acetone, CO , and NH_3 values include loadings from other sources previously discussed.

METABOLIC PRODUCTS (8-MAN CREW)

Contaminant	TIME to $\frac{1}{2}$ SMAC (Days)
CO	6.9
NH ₃	2.1
Acetone	76
Ethanol	8.1
Methyl Mercaptan	14
Ethyl Mercaptan	14
Propyl Mercaptan	14
Pyruvic Acid	1.0
Indole	0.7
Skatole	1.2

Fire

An unusual odor and crew headaches occurred on Shuttle flight STS-6. Burnt wire insulation from an electrical short was the suspected causal agent.⁹ Electrical fire can produce a number of noxious agents including halogenated organics, benzene derivatives, nitriles, and cyanates.²² Space Station design must be able to handle such contingencies either through the TCCS or a smoke removal unit,²³ without having to rely on venting the cabin air to space and repressurizing. The trace gas monitoring system should be able to detect and quantify contaminants representative of those generated by an electrical short or fire.

To ascertain monitoring needs following a combustion incident, the hypothesized concentrations of pyrolysis products after a fire and their corresponding SMACs were used to estimate a factor proportional to monitoring importance.

Contaminant	Concentration ²³ (PPM)	SMAC (PPM)	Concentration/SMAC
CO ₂	10,000-100,000	5,000	2-20
CO	3,000-30,000	25	120-1200
HCN	5-100	1	5-100
HCl	5-100	1	5-100
NO ₂	1-100	0.5	2-200
H ₂ S	1	2	0.5
SO ₂	100	1	100

Although the concentration of pyrolysis products vary widely from fire to fire, smoke detectors provide adequate warning of toxic products, since smoke is generally produced in copious amounts. Analysis of fire reports involving death or serious injury where smoke detectors have been installed show that the detector was inoperative or evacuation was not possible.

Investigation of fire fatalities have shown CO to be the primary toxicant with HCN often present in toxic quantities. However, documented cases of HCN being the primary toxicant are rare.²⁴

Of the toxic gaseous products presented above, CO is expected to exist in highest concentration relative to its SMAC, therefore, if CO is below its SMAC value then the other toxic products would likely be also. Because of the uncertainty of predicting the concentration of pyrolysis products after a fire, monitoring should be considered for other toxic products as well: HCN, NO₂, HCl, and SO₂. Although no specific data could be found on the production of COCl₂, HF, COF₂, and short chain aldehydes, contingency monitoring should be considered because of their toxic and corrosive action.

For fire safety concerns, CO₂ will be used for fire suppression, followed by venting cabin air to space and repressurizing. Smoke detectors are an integral part of the fire detection and suppression system. To protect from toxic combustion products, infrared monitors have been previously recommended for CO, hydrogen fluoride (HF), and hydrogen cyanide (HCN).²⁵

Volatiles will be released to the atmosphere from electrolysis and from phase change urine processing. Carboxylic acids and phenols will be major contaminants.^{26,27} Iodination products from the water disinfection process may cross the air/water interface and permeate the life support environment. The identity of these products, their expected concentrations, and their medical effects are largely unknown.²⁸ However, the byproduct concentrations and effects of iodination are probably less than those resulting from chlorination.

CONCLUSIONS

The monitoring system for Space Station Freedom must be adaptable to accommodate new parameters and concentration ranges. All agents should be monitored that have a reasonable probability of occurrence at or above some action level, such as $\frac{1}{2}$ SMAC. This would include the capability to monitor for toxics after a fire or spill so a pressurized element could be declared safe for entry or for removing protective gear donned during an incident. The analytical method relied upon must be able to quantify at action level concentrations. The basis for monitoring should be the contaminants: toxicity, quantities or production rates, removal efficiencies of the ECLSS system, and capacity to poison the ECLSS system. The importance for monitoring is increased by the relatively low air flow rate through the TCCS and high reliance on the TCCS for contaminant removal.

Continuous monitoring of cabin return air is required for major components and those critical for life support. The minimum

monitoring effort should include continuous monitoring for: N₂, O₂, CO₂, CO, H₂O, H₂, CH₄, non-methane hydrocarbons, aromatics, and halocarbons. There should be a sample line to each module routine comparison of atmospheres from remote sections of the spacecraft.

A monitor or probe will be needed in the EVA airlock for analysis of propellants: N₂O₄, hydrazine, and monomethyl hydrazine.

Other chemicals targeted for routine monitoring include: Freon 12, HCl, HCN, NH₃, O₃, NO₂, H₂S, HF, formaldehyde, Halon 1301, toluene, acetaldehyde, ethanol, acetone, dichloromethane, glutaraldehyde, trimethylamine, benzene, o-diethylphthalate, propylfluorosilane, 2-methylhexane, acrolein, methanol, vinyl chloride, isopropyl alcohol, allyl chloride, isobutyl alcohol, chlorobenzene, n-butyl alcohol, isobutylene chloride, cyclohexanol, trichloroethylene, n-butylaldehyde, tetrachloroethylene, hexanal, methyl ethyl ketone, heptanal, methyl isobutyl ketone, m-xylene, cyclopentanone, indene, methylheptanone, propylbenzene, isobutyl ketone, p-cymene, acetonitrile, ethyl cellosolve, nitromethane, butylacetate, mercury, furan, trimethylsilanol, sylvan, p-dioxane, ethylacetoxycetate, tetramethyl-1,2-epoxyethane, methyl mercaptan, ethyl mercaptan, propyl mercaptan, pyruvic acid, indole, and skatole.

The chemical list can be refined by considering the removal efficiencies of the ECLSS and by assigning SMAC values to those compounds for which a value of 0.1 mg/M³ was assumed. Also, an evaluation by toxicological effects category should be done to address additive effects. The above list was determined by considering independent action only, and more than one contaminant will be present.

Each experiment and manufacturing process must be evaluated in great detail for possible sources of cabin contamination. Lab facilities will be sources of biologicals, combustion and oxidation products, acid gases, metal and crystal fumes, and assorted lab wastes. The lab racks should be equipped with monitoring devices specific to the process being contained. The chemical storage area should also be equipped with a monitoring probe.

Finally, sample collection and preservation will have to be continued for ground based analyses, to confirm the accuracy and reliability of the onboard monitoring system.

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