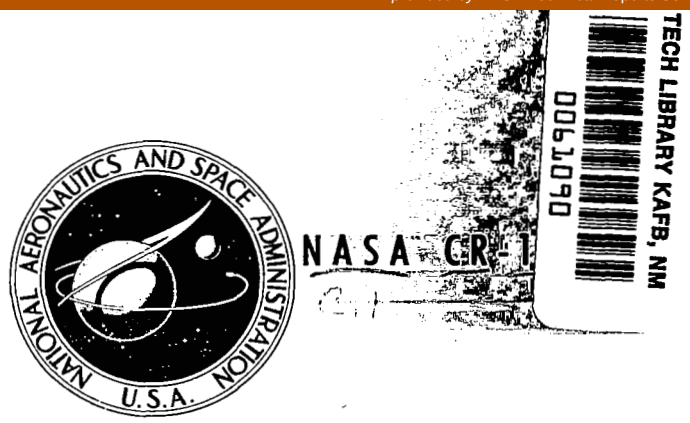

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UNIVERSITY ROLE IN ASTRONAUT LIFE SUPPORT SYSTEMS: MONITORING ATMOSPHERIC CONTAMINANTS

by H. L. Galiana

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16. Abstract

Substances toxic to man can accumulate in the atmosphere of a "closed" environment, whether industrial, submarine or in space.

This report concentrates on the state of the art in monitoring techniques for biological and chemical atmospheric contaminants. Brief reference is made to currently accepted allowable contaminant concentrations. An attempt is made to point out areas where there is a need for more research especially suited to graduate school laboratories. Such research should prove invaluable when extended from space capsule to Earth pollution problems.

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FOREWORD

The Environmental Systems and Effects Division of the National Aeronautics and Space Administration's Office of Advanced Research and Technology is vitally interested in fostering and developing new ideas which will advance the technology of life support and astronaut protective systems. Many excellent ideas and operating systems have been brought to fuition in NASA laboratories and by associated contractors. However, involvement of academic laboratories and personnel has not been as great as was originally hoped. Perhaps this has been due to the fact that academic personnel were not aware of the critical problem areas in life support and protective systems, nor were they cognizant of the fact that NASA is interested in joining with colleges and universities to develop new ideas to solve future space flight problems.

This brochure on Atmosphere in Life Support Systems is intended to introduce you to some of the existing technology involved in keeping crews alive in spacecraft and in the extravehicular environment and to pinpoint areas where problems exist. We encourage you to study this brochure. If in your research, you have already developed new ideas, theories, chemicals, etc., which would be applicable to NASA's effort, we hope you will feel inclined to contact us to see whether a joint research effort can be initiated.

Walton L. Jones, M.D.
Director, Environmental
Systems and Effects Division

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I. INTRODUCTION

Substances toxic to man can accumulate in the atmosphere of a "closed" environment, whether industrial, submarine or in space. These toxic substances can be generated by outgassing of system components, leakage from chemical processes or by the enclosed men themselves. The presence of such atmospheric contaminants, especially in the space capsule, requires

i) the determination of threshold limit values (TLV) and maximum allowable concentrations (MAC) for all potential toxic contaminants based upon prolonged exposure of experimental subjects, as well as engineering controls over intravehicular materials and processes;

ii) the provision of means of detecting toxic biological and chemical contaminants, and associated warning systems to assure that the MAC's are not exceeded;

iii) the presence of systems to continuously remove and control both chemical and biological contaminants;

iv) the provision of necessary gas stores, valving, etc. for planned decompression to remove accumulated toxic contaminants in an emergency.

This report will concentrate on a review of detection methods with a brief section on presently accepted contaminant air concentration limits. It will attempt to point out those areas where there is a need for continued research especially suited to university laboratories. This should lead to the

development of lighter, safer and more reliable automatic monitoring techniques for atmospheric contaminants. The potential applications of such methods to the monitoring and automatic control of medical, civil and industrial environments is obvious.

II. NATURE OF CONTAMINANTS AND ALLOWABLE CONCENTRATIONS

2.1 Trace Chemical Contaminants

Trace chemical contaminants are defined here to be any non-biological constituents of the atmosphere, excepting oxygen, the diluent if any, carbon dioxide and water. Unless there is a fire or major system failure, these constituents usually have very small concentrations (ppm→ppb), hence the term "trace" contaminants.

Spacecraft contaminant sources are materials, processes and men. Materials may generate contaminants by off-gassing into the spacecraft atmosphere. This requires careful testing and selection of materials to be used in components inside the spacecraft (1, 2, 3, 4). Contaminants may also be generated by the operation of life support subsystems. Examples are leakage of ethylene glycol from a heat exchange system, hydrogen from a battery or fuel cell, and methane or carbon monoxide from an oxygen reclamation system. Finally, a great variety of contaminants can be generated by the enclosed men themselves. A partial list of such products of human activity is given in Table 1 (2, 5, 6, 7, 8).

Hundreds of compounds have subsequently been identified in analyzing atmospheric samples of closed systems (5, 9, 10, 11, 12, 13). Some of these contaminants are not toxic to man in themselves. However, their presence is hazardous in that their degradation or chemical reaction by-products may be toxic, or cause deterioration in cabin materials and

Table 2.1

Contaminants Generated by Man

Respiration	Skin	Lower Intestine
Acetone	Body proteins	Indole
Ethyl carbonic acid	Fatty acids	Skatole
Methane	Waxes	Ammonia
Carbon monoxide	Sugars	Phenols
Hydrogen	Phenols	Hydrogen sulphide
Ethyl alcohol	Urea	Amines
Methyl alcohol	Utric acid	Urea
2-Butanone	Lactic acid	Hydrogen
Acetonitrile	Triglycerides	Methane
	Inorganic salts	Carbon monoxide
	Trace vitamins	

processes.

The air concentrations to be discussed below are those proposed in the report of the Panel on Air Standards for Manned Space Flight of the Space Science Board, National Academy of Sciences (13). The Panel reviewed reports of the analysis of atmospheric contamination in manned space flights, ground-based simulations of cabin atmospheres, nuclear submarines, Sealab experiments, and the analysis of off-gas products and cabin materials. Some 200 contaminants were singled out as possible space cabin contaminants, though only a small proportion are expected to reach levels of concern.

Some of these contaminants had already been studied by the National Academy of Sciences - NRC Committee on Toxicology - who recommended limits for 60-minute emergencies and 90-day continuous exposures in submarines (14, 15, 16). The Panel recommended that these limits be adopted as guides for emergency and 90-day exposures in space cabins. However,

further studies are needed before extending these limits to 1000-day missions in the unusual conditions of space flight.

Of the remaining contaminants, NASA requested that limits be proposed for 90-day and 1000-day missions in space for ten contaminants, and emergency exposure limits for five contaminants. The provisional maximum allowable concentrations presented by the Panel are shown in Tables 2 and 3. All the values represent ceiling concentrations except for carbon monoxide where the stated value is the maximum allowable integrated level over 12 hours (17, 18, 19). In the case of emergency exposures, the limits were chosen to avoid interference with the performance of a task or cause irreversible injury to an astronaut, although transient effects may be experienced.

Table 2.2

Provisional Emergency Limits

for Single 60-min Exposures

in millimoles/25 m^3 ≡ ppm at 25° C and 1 atm.

Contaminant	Limit
2-Butanone	100
Carbonyl Fluoride	25
Ethylene Glycol	100
2-Methylbutanone	100
1,1,2-Trichloro, 1,2,2-Trifluorethane and related congeners	200

The limits for continuous exposures were derived from levels producing the earliest signigicant toxicological response with the most sensitive measures available to date, applying a safety factor varying with the nature of the toxic effect.

Table 2.3

Provisional MAC's for Continuous Exposures

in millimoles/25 m^3 ≙ ppm at 25° C and 1 atm.

Contaminant	90-day	1000-day
n-Butanol	10	10
2-Butanone	20	20
Carbon monoxide	15*	15*
Chloroform	5	1
Dichloromethane	25	5
Dioxane	10	2
Ethyl acetate	40	40
Formaldehyde	0.1	0.1
2-Methylbutanone	20	20
Trichloroethylene	10	2
1,1,2 Trichloro, 1,2,2-Trifluoroethane and related congeners	20	no recom.

* integrated level over 12 hours

The limits presented in the Panel's report are provisional and subject to revision for the following reasons:

i) Inadequate or incomplete toxicological information for many of the detected contaminants, in single or multiple compound long-term exposures.

ii) Inability to accurately predict effects of reduced atmospheric pressures, stress, 0-g, varying O_2 concentrations, confinement, etc. on the toxicology of a given contaminant.

iii) Possible synergistic effects among chemicals.

Furthermore, the exact nature, number and generation rates of contaminants in a spacecraft remain to be specified, since they depend on the final choice of life support systems and cabin materials for a particular mission (20, 21). This will in turn affect the choice of contaminant monitoring technique(s) to verify the efficient operation of the contaminant control systems. For example, in the case of the proposed Regenerative Advanced Integrated Life Support System (AILSS), a representative list of expected major contaminants is presented in Table 4, together with currently accepted MAC's predicted generation rates, and toxic effects (20).

Table 2.4

Major AILSS Contaminants (500 days - 9 men)

* I ≡ irritant, N ≡ narcotic, B ≡ blood poison, A ≡ asphixiant

Contaminant	Production Rate (lb/hr) Biological	Equipment	MAC (ppm)	Main Toxic Effect*
Acetaldehyde	8.24×10^{-8}		40	I
Acetone	1.82×10^{-7}		200	N
Ammonia	2.36×10^{-4}		10	I
Benzene		1.44×10^{-5}	5	N,B
n-Butanol	1.08×10^{-6}		10	N,I
Butyric acid	6.22×10^{-4}		8	I
Carbon monoxide	9.20×10^{-6}	1.08×10^{-5}	15	B
Cyclohexane		1.30×10^{-6}	60	N
Dichloro-difluoromethane		3.60×10^{-5}	200	N
Ethanol	3.31×10^{-6}		100	N,I
Hydrogen	7.27×10^{-6}	2.91×10^{-5}	10000	A
Hydrogen sulphide	4.15×10^{-9}		2	I
Methane	1.17×10^{-4}	2.52×10^{-5}	13000	A
Methanol	1.25×10^{-6}	1.78×10^{-5}	40	N,I
Methylene chloride		3.60×10^{-5}	100	N
Pyruvic acid	1.73×10^{-4}		0.5	I
Toluene		1.20×10^{-5}	40	N,B
Vinyl chloride		9.90×10^{-5}	100	N

Recommendations for University Research

1. Continued and expanded research to determine or validate 90-day and 1000-day limits for continuous exposures, especially with sub-human primates, or from industrial exposure studies.

2. Research into possible synergism among contaminants and environmental conditions, which might alter the effective toxicity of multi-component air mixtures in space.

3. Detailed studies into the basic toxic mechanism of some of the most important contaminants. This should help determine the exact nature of the injury, its reversibility, and the net rate of accumulated damage, for various exposure levels.

2.2 Biological Contaminants

A partial list of those biological contaminants normally associated with man is given in Table 2.5. These and other organisms may be trapped in cabin materials, or originate from the astronaut's nose, throat, skin, intestines and associated secretions (22,23,24). They can themselves be hazardous to health, produce toxic or obnoxious byproducts, or foul and deteriorate the operation of equipment if allowed to grow.

Table 2.5

Partial List of Biological Contaminants

Bacteria		Fungus	Viruses
Aerobacter	Mima	Aspergillus	Advenovirus
Alcaligenes	Pseudomona	Candida	Hepatitus
Bacillus	Salmonella	Cryptococcus	Herpes virus
Bacteroides	Sarcina	Geotrichum	Mycoplasma (PPLO)
Clostridium	Shigella	Mycoderma	Myxovirus
Escherichia	Staphylococcus	Saccharomyces	Picornavirus
Gaffkya	Streptococcus	Trichophyton	Reovirus
Lactobacillus	Xanthomona		

The viruses, rickettsiae and PPLO's are not expected to multiply outside the human body, though they may remain viable in the cabin for significant periods of time; they range from 200°A to 1.5 μ in size. The bacteria and fungi, on the other hand, can grow in the most meager supply of substrate on surfaces or in aerosols; the bacteria range from 0.5-10μ and the fungi from 1-20μ up to the visible multicellular molds.

The level and quality of biological contamination to be expected in the cabin air during long term space flights is still not well defined. Clean room and space test chamber studies do not have consistent operating conditions and, in any case, they cannot simulate the effects of weightlessness and radiation in space. However there is general agreement in the observed transfer of microorganisms between subjects and alterations in skin and oral microflora (28,30,31). Whether there is a marked increase or decrease in the number of airborne microorganisms is still controversial, probably because the control procedures were different

in each study (25,26,27,28,29). Space-type diets and various environmental atmospheres can in themselves alter the number and types of indigenous flora in a man (30,32).

Actual space flight microbiologic studies have been limited to examinations pre- and post-flight of the astronauts and of waste samples stored in flight. Though there is great variance among individuals, it is generally concluded that the space flight conditions result in a transfer of microorganisms between the men, and a simplification of the microflora: the growth of gram-positive organisms (e.g. staphylococcus aureus and beta streptococci) is enhanced, while that of certain organisms in the anaerobic flora is inhibited (33,34,35,36). There has been no in-flight monitoring of airborne and surface biological contamination.

Furthermore, the environmental factors of space flight and their associated stresses on the astronauts (O-g, radiation, high accelerations, etc.) may increase their susceptibility to disease. Also, normally harmless microorganisms may become highly pathogenic in a disturbed man-microflora ecology. So far immunologic examinations of the astronauts pre- and post-flight do not indicate any significant changes (35,36). However, animal experiments point toward an increased hazard of infection and slower rates of healing or recovery (26,37,38). A better understanding of the "normal" man-microorganism ecology is needed to minimize the danger of illness in space.

Since so little is known about the characteristics of biological contamination in the space cabin, it is difficult to decide which organisms should be regularly monitored in-flight, and almost impossible at this time to set "safe" contamination levels for expected dominant species. The answer for the moment is to keep the cabin air as free of microorganisms as possible via filters and catalytic burners, and institute a biological monitoring system to detect the level and identity of as many biological contaminants as possible. Such data, together with further studies into the mechanics of disease in space, should lead to the determination of a safe biological environment. A sterile environment may not necessarily be either possible or desirable.

Table 2.6

Expected Airborne Biological Contaminants

Actinomycetes
Alcaligenes faecalis
Bacillus spp.
Beta streptococci
Corynebacterium spp.
Escherichia coli
Flavobacterium
Gaffkya spp.
Lactobacillus
Micrococcus spp.
Mima polymorpha
Pseudomonas achromobacter spp.
Sarcina spp.
Staphylococcus epidermidis and aureus
Xanthomonas translucens
Yeasts, molds

A review of microbiologic studies (27,33,35,39) suggests that those microorganisms listed in Table 2.6 are representative of the major contaminants expected in a space cabin atmosphere. This is only a tentative

list since space flight factors may alter the findings of Earth-based studies, especially in long-term habitation of a relatively small capsule.

Recommendations for University Research

1. Further studies on man and his indigenous flora, especially aimed toward a better understanding of endogenous disease and its treatment (40,41).

2. Determining bacteriologic standards for space cabin atmospheres.

3. Continuation of chamber studies (with men or animals) to determine relation between susceptibility to disease and environmental factors.

4. Use of mathematical models to investigate the ecology of microorganisms and man, predict possible mechanisms for the transmission and evolution of disease in space, etc.

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III. TRACE GAS MONITORING TECHNIQUES

Trace monitoring includes three steps: sampling, instrumentation, and data correlation or interpretation. We will mainly consider here on-line techniques to continuously monitor the trace gas atmospheric contaminants. Other preconcentration and sampling techniques (e.g. cryogenic traps, filter beds...) are discussed in many references (2,3,4, 5).

The monitoring instrumentation should be sufficiently specific and sensitive to detect large numbers of trace contaminants in the atmosphere, at a great enough sampling rate to detect malfunctions or failures early. Those methods with the greatest potential are described below.

3.1 Gas Chromatography

Gas chromatography is especially attractive because of its capability to identify and quantify large numbers of contaminants without prior separation. It has been widely used to analyze contaminants eluted from cryogenic traps or adsorption beds in closed system tests and space cabins post-flight (2,3,4,5,6).

A gas chromatograph consists mainly of a column packed with either absorbant material such as silica gel or molecular sieve, or a solid support such as crushed firebrick

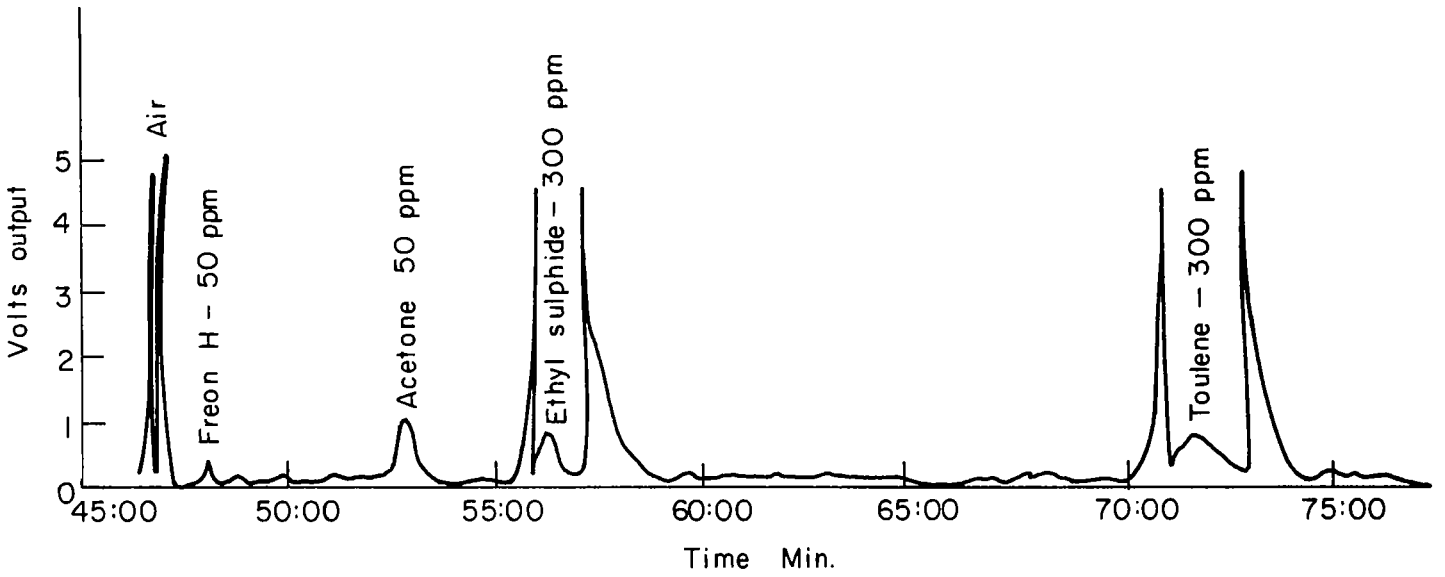

Fig. 3.1 Typical Gas Chromatogram (column 3, Ref. 15)

lightly crated with a high-boiling partition liquid. A carrier gas, usually helium, passes continuously through the column. When a gas sample is injected into the carrier gas stream, individual constituents are preferentially absorbed in the column, approximately in the order of their boiling point and/or molecular weight. Thus the constituents are eluted from the column each at a specific time. The eluted components can be measured by one of several types of detectors placed at the end of the column, e.g. flame ionization, cross-section ionization, breakdown voltage ionization, thermal conductivity.... The magnitude of the detector response is a measure of the concentration of the eluted constituent. Several columns can be used in series or in parallel to increase the number of gas constituents which can be separated and identified. Thus, a gas chromatograph can provide both a qualitative and a quantitative analysis of a gas sample (7, 9).

Several gas chromatograph configurations have been developed. Most are large, complex systems designed for laboratory use and applications to off-line analysis of contaminant samples from submarines or closed system tests. Such systems can detect and quantify as many as 100 contaminants. Miniaturized, flight-tested models are usually restricted to preprogrammed monitoring of some 30 contaminants. Depending on the column-detector combinations used, some of the models were designed for application to lunar and martian atmospheric or soil studies on unmanned flights (6, 11, 13),

and ranging in sensitivities from 10^{-9} to 10^{-13} moles concentration.

Others were specifically intended for manned space flight atmospheric monitoring of the cabin (14,15). Those concepts using a mass spectrometer as a sensitive detector in gas chromatography are discussed in sect. 3.2. One system developed for the Manned Spacedraft Center (NASA) uses three columns and associated corss-section ionization detectors. It has a volume of approximately 800 cu. in. (not including He storage(, weight of 12 lbs. and a power consumption of 10-8W. It can sample the atmosphere every 80 min. for 14 gas constituents down to 10 ppm, and can operate continuously for 20 days, using helium stored at 6,000 psi in a 5.9" diameter titanium sphere (14). In its limited unmanned flight tests, it was plahued by valve problems.

Work is under way to improve the sensitivities of gas chromatographic detectors (6, 9 , 10, 11) but it is very difficult to achieve 0.1 ppm sensitivities unless a mass spectrometer is used as the detector (see sect. 3.2). However, though such a concept is attractive it increases the complexity of the system and decreases its reliability.

The following disadvantages are usually common to gas chromatographic techniques:

--- The required helium storage increases the weight and volume penalty of the system, is a safety hazard, and limits the operation life-time.

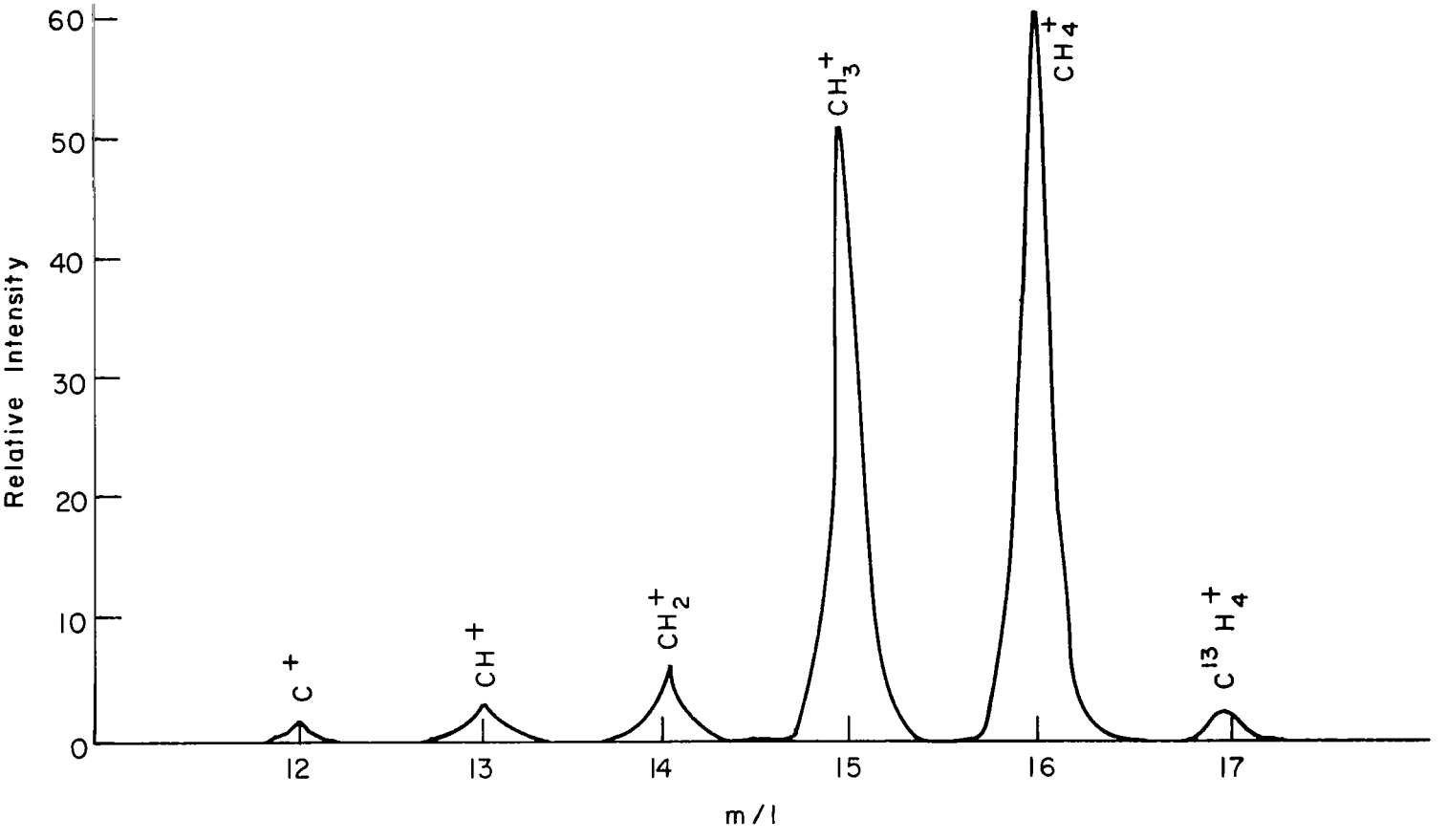

Fig. 3.2 Typical Mass Spectrum for Methane

--- Complex flow controls are required to handle the helium and atmospheric samples, reducing system reliability.

--- Column sorber materials are subject to aging or degradation such that regular calibration or replacement is necessary.

--- There is no positive means of identification if an unknown contaminant appears for which the system has not been preprogrammed. Its identity can only be determined using a lengthy calibration procedure, or by comparing the retention times in the different columns and referring to previous data and experience.

Nevertheless, at the present time, gas chromatography appears to be the most versatile and flight-qualified technique for "on-line" monitoring of 30 contaminants in concentrations as low as a few ppm.

3.2 Mass Spectrometry

A mass spectrometer consists principally of a sample introduction system, an ion source, a mass analyzer and an ion detector. It requires a near vacuum for its operation (preferably less than 10^{-4} torr) but this is readily available from outer space in a spacecraft. In summary, a sample of gas is introduced and ionized by, for example, electron impact, photoionization or field ionization. The result is the production of ions of various mass-charge ratios, which can in turn be separated using magnetic deflection, in time of flight, radiofrequency or other types of mass analyzers. A spectrum of the relative abundance of ions of differing mass-charge ratios can then be measured by the ion detector(s), usually of the electron multiplier type (1, 6, 16, 17).

In a given instrument, each gas has a characteristic mass spectrum or fragmentation pattern. The complexity of this spectrum is strongly dependent on the type and intensity of ionization used, increasing as the efficiency of ionization increases, due to isotopes, dissociation, fragmentation of original particles,...etc. This is a problem in the analysis of a mixture of gases, especially in trace quantities, where the observed spectrum is a superimposition of the individual complex constituent spectra. Unfortunately a reduction of spectrum complexity in an instrument, though it leads to improved qualitative identification of gas constituents, also leads to a decreased sensitivity in the quantitative determinations. Thus, though laboratory mass spectrometers are available with resolutions of 100,000, sensitivities as low as a ppb and

and response times of the order of a few milliseconds, these properties are not all available in the same instrument. Because of size restrictions, the resolution of most flight spectrometers is of the order of 100, with sensitivities in the neighborhood of a ppm.

Many flight qualified mass spectrometers have been developed, mainly intended for use as specific or major atmospheric constituent monitors (18, 19). One such system can monitor O_2, N_2, H_2O and CO_2 every 2 sec (20); it has a volume of 167 cu. in., weight of 6.5 lbs. and maximum power consumption of 3.7 watts. Work is also underway to perfect and miniaturize mass spectrometers (21, 22, 23) to the point where flight qualified double-focusing spectrometers, suitable for incorporation into trace contaminant monitoring systems, weigh less than 10 lbs.

Though blessed with fast scanning rates, high sensitivity and operation life-times only limited by the shelf-life of enclosed electronics, most mass spectrometers still suffer from the following major disadvantages:

---Complex mass spectra requiring the use of a computer to solve multiple linear equations of the form,

$$I_1 = A_1x + B_1y$$
$$I_2 = A_2x + B_2y$$

where I is the peak intensity of each mass of interest, A and B are the pattern coefficients for pure components (obtained by calibration), and x and y are the desired concentrations of two components in this case. This type of analysis leads to inaccuracies, especially for trace quantities of gaseous

contaminants which must be measured in a background of hundreds of other possible contaminants.

---The stability of the instrument is not very good, requiring regular calibration. This is due to changes in the ion source characteristics and to surface contaminations in the presence of oxygen.

The first disadvantage can be alleviated by using the mass spectrometer as a sophisticated detector in a gas chromatograph (24). This provides accurate, low level (1 ppm) monitoring of separated atmospheric contaminants with much greater versatility than either system alone. However the system complexity is increased,decreasing the over-all reliability, and frequent calibration is still required. Furthermore, no such hybrid system has yet been miniaturized or flight qualified, though the technology is sufficiently developed to do so and such laboratory models have been used in life support simulation tests (2, 3, 24).

Another system has recently been developed where the best properties of gas chromatography and mass spectrometry are combined into a hybrid sensor (25, 26). Temperature programmed column sorber materials are used to preconcentrate the trace contaminants, thus increasing the sample quantity and allowing a decrease of ionization potential without loss of sensitivity. The resulting simpler mass spectra, appearing separated in time, can be analyzed by computer. The detector and ion source stabilities are improved by precutting the air from the sorber beds before desorbing into the spectrometer, so that the major atmospheric constituents (O_2, diluent)

are not monitored. The air carries the atmospheric sample through the beds, removing the requirement for stored helium that exists in gas chromatography. A laboratory prototype has been built and tested, and found capable of monitoring some 60 contaminants, at concentrations from 0.5 to 10 ppm, approximately every 1 1/2 hours. It is expected that a flight qualified miniaturized instrument would be feasible with weight and power penalties of approximately 15 lbs. and 20 watts. The operation life time of such an instrument should only be limited by that of its electronic components and sorber beds.

3.3 Spectrophotometry

In spectrophotometry, molecules are identified by their characteristic absorption (attenuation) spectrum of radiation in the ultraviolet, visible or infrared regions. A sample of gas absorbs energy at many discrete and characteristic wavelengths of the irradiating spectrum. These absorption bands are due to rotational transitions of the molecule in the far infrared, to excited vibrations between atoms and groups of atoms within the molecule in the near and middle infrared, to energy state transitions in the outer electrons of the molecule's atoms in the visible and ultraviolet regions. For a given radiation path length, the intensity of these bands is proportional to the partial pressure of the gas. Thus absorption spectra can be used for both qualitative and quantitative measurements on gas mixtures. Unfortunately this technique has the same superimposed, complex spectra analysis problems as mass spectrometry, with the additional problem of a varying

baseline caused by changes in the light source, detector and background absorption of gases not measured (1, 27, 28, 29).

This is alleviated slightly by usually measuring spectra for mixtures of trace gases in the near infrared (2-16μ) where the best combination of selectivity and detectability is found. Here we often find wavelengths at which absorption is characteristic to a single gas (e.g. CO_2 at 4.3μ). Also, in this range, oxygen and nitrogen are transparent. If many gases absorb at the same frequency (wavelength), then equations of the form below must be solved,

$$A_i = k_{1i}C_1l + k_{2i}C_2l + \ldots k_{ji}C_jl, \; i = 1, \; \ldots j$$

where A_i is absorption at i^{th} frequency (measured by detector)

k_{ji} is absorption coefficient at i^{th} frequency due to j^{th} compound (by calibration)

l is path length of radiation

C_j is desired concentration of j^{th} compound

This equation is valid for small C_j, as is expected in the case of trace contaminants in the space cabin atmosphere.

All absorption spectrophotometers have in common a source of electromagnetic energy and a detector which receives a portion of this energy after it has passed through a gas. They differ in the manner in which the radiation is separated into component wavelengths and recorded.

In dispersive spectrophotometers, the incident radiation is separated according to wavelength, using a prism or diffracting grating, and only a very narrow frequency interval reaches the detector at any time. The full spectrum is scanned by varying a geometrical factor such as a mirror angle. However

such systems are bulky, delicate and require very long optical path lengths to reach ppm sensitivities, due to poor S/N ratios and the reduced radiation level passing through the gas at any one time. They are usually restricted to laboratory studies or monitoring space cabin simulation studies .

Some non-dispersive types of spectrophotometers have been developed and flight-qualified to monitor specific gases in space flight. Tremendous size reductions are achieved by using specific wavelength filters to measure background and gas absorption. For example a single-beam, dual-wavelength filter photometer has been developed to monitor CO_2. The unit weighs less than 2.7 lbs., occupies about 40 cu. in. and draws less than 1 W of 28 V power. Its operation is continuous and automatic (30, 31). This approach has been extended to the development of two-gas atmosphere sensors using ultraviolet and infrared channels: continuous and automatic measurements on O_2, CO_2, N_2 and H_2O are possible with a package of less than 5 lbs. (31).

However, dispersive spectrophotometers do not appear attractive at the moment to monitor a large number of trace contaminants in the space cabin atmosphere. Further research might change this picture: for example the sensitivity and size penalties might be significantly improved by the use of a laser as the source of electromagnetic energy, with its radiant beams of high power, spectral purity and very small beam divergence.

The second major type of spectrophotometer is the interferometer spectrometer. Interference spectroscopy uses the principle of constructive and destructive interference of

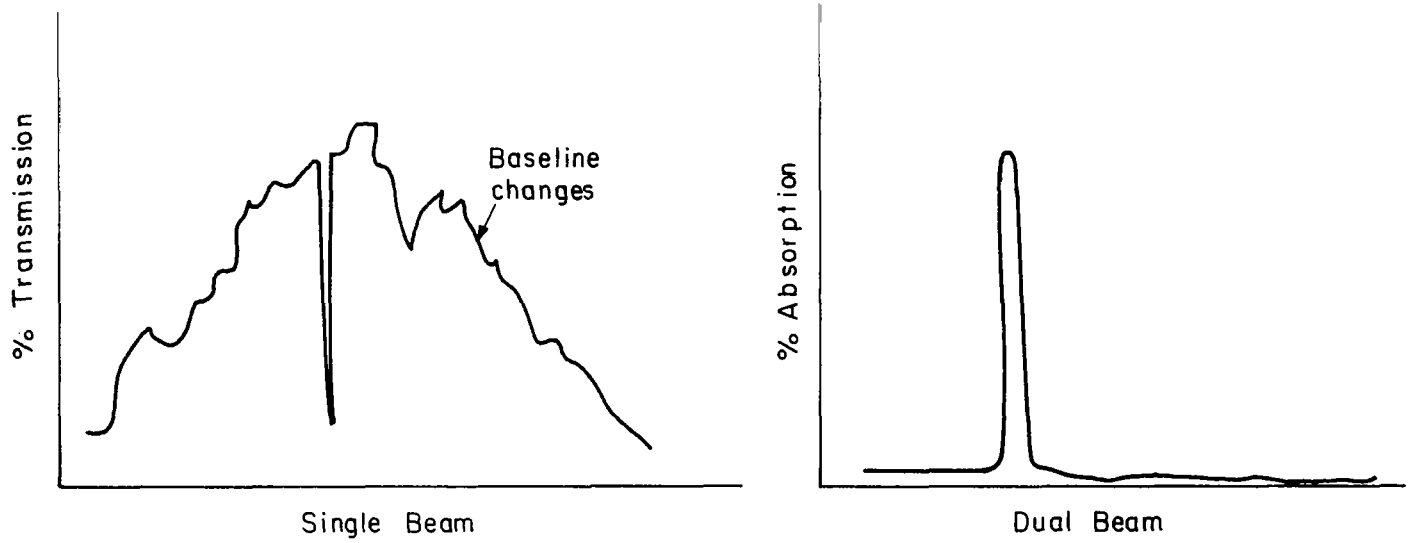

Fig. 3.3 Single and Dual Beam Spectra

light waves. Radiation of all frequencies enters the interferometer and is measured simultaneously at the detector. Thus the detector output is actually a Fourier transform of the desired intensity vs frequency spectrum. However the interferogram can easily be processed by analog or digital means to produce the inverse Fourier transform and with it the absorption spectrum. Several advantages compensate for the increased date manipulation (32, 33, 34);

--- The multiplexing process yields an increase in S/N ratio of $\sqrt{M}$ over comparable dispersion instruments, where M is the number of resolution elements (monitored gases).

--- The elimination of entrance slits or diffraction gratings and the use of larger cones of radiation decreases the size of the instrument, increases its sensitivity by 100-1000, and thus allows for fast scanning rates (every sec.) even in the case of trace contaminants.

--- The faster scanning rate also allows for digital or analog sequential addition of interferograms before processing, producing a S/N ratio enhancement of $\sqrt{n}$, where n is the number of successively added scans, and if desired, the subtraction of unwanted background interferograms if they can be obtained (e.g. in dual beam instrument).

--- Monitoring the absorption of specific gases at characteristic frequencies only requires the use of a tunable filter (or several fixed band-pass filters) to process the interferogram, without loss of the full scan. This processing could also be done by digital means for greater versatility.

Furthermore, interference spectrometry, contrary to gas chromatography or mass spectrometry, has the advantages of continuous, automatic and passive measurements on a space cabin atmosphere, with a lifetime only limited by that of the electronics. One such laboratory system has been developed and tested with 43 compounds: 10 binary, 10 trinary, five 5-order and one 15-order mixture (35). Sensitive in the 1-40 ppm range, with a resolution of $30cm^{-1}$, it can provide a complete atmospheric scan every 2-5 min. in the near infrared spectrum 3-16μ. A proposed dual beam system with an effective path length of 10 m (20 reflections over 0.5 m) would easily reach sensitivities in the ppb range, with a resolution of $10cm^{-1}$. In this case the output absorption spectrum would be a measure of the deviations of the actual cabin atmosphere from a desired reference atmosphere in a gas cell, and variations in source and detector characteristics would be cancelled out. A laboratory prototype is expected to weigh 84 lbs., occupy 10,000 cu. in. and consume 100 W. However, miniaturization for a flight instrument is expected to greatly reduce these penalties and make it competitive with gas chromatography or mass spectrometry.

A slightly different, but even more interesting, approach which is being investigated is the application of Raman spectra to trace measurements (36). Here a source of monochromatic light (e.g. laser) irradiates the gas in the beam path, and the resultant photon frequency spectrum (different from the incident frequency) is characteristic to the gas constituents. This method should easily be sensitive in the ppb range and

and greatly reduce complexity, weight and volume penalties; more research should be encouraged.

3.4 Microwave Spectroscopy

Microwave spectroscopy has been largely developed for use in research and laboratory analysis. It is similar to the optical spectrometers mentioned above, in that a source of electromagnetic energy radiates through a gas sample and the resulting absorption spectrum is characteristic to the gas constituents. The frequencies involved are in G H_z and the absorption lines result from changes in the molecular rotation states of polar molecules only (37, 38). However there is no need for dispersive or interference techniques; the source itself, being electronic, can easily be swept through the desired frequency range.

The spectra obtained may be extremely complex (hundreds of lines for one molecule) but very specific, and resolutions of 0.0001 cm^{-1} are possible. Quantitative determinations are facilitated by the fact that the maximum signal absorption at a particular frequency due to a particular gas is directly proportional to the partial pressure of the gas and is unaffected by the total sample pressure or composition.

Present day microwave spectrometers are bulky, requiring very long path lengths (several meters) of radiation to achieve ppm sensitivities. Only laboratory models have been developed and they usually occupy a large part of an average sized room. (However, NASA is concerned with the development of portable microwave spectrometers.) Also, there is a poor trade-off

between scan rate, and resolution/accuracy. The greatest resolution and detectability is obtained at very low sample pressures (.01 torr), but this also requires very long scanning time (several days) to get a full spectrum. However, full spectrums at maximum resolution are not required for all analyses.

Despite these disadvantages, including the required manipulation and pumping of atmospheric samples, this technique may prove extremely useful in the future as a research tool in orbiting platforms or planetary bases. Its primary advantage is versatility since the scan time and spectral resolution can be adjusted to many analytical requirements, automatically, through suitable computer control and analysis. Improvements in detector sensitivities and absorption cell designs could lead to a reduction in volume penalties. Research should also be continued to expand the catalog of available microwave gas spectra.

3.5 Liquid Crystals

Although only in the research stage, this technique is presented as an example of the application of a new approach to trace contaminant measurements. Its merits remain to be evaluated but it is hoped that it will stimulate other new ideas.

Toliver et al. studied the application of liquid crystals to trace contaminant detection and quantification in space cabin atmospheres (39). Trace contaminants generate a colour response in cholesteric liquid crystals. A new molecular species, 3 Beta-Carboxy-5-Cholestene, specific for

aliphatic and aromatic acids, was considered. A Bausch and Lomb High Intensity Monochromator illuminated the liquid crystal, and the scattered light output was measured by a photomultiplier. Upon exposure to a given trace contaminant concentration, the wavelength of maximum reflection was obtained by adjusting the monochromator to the wavelength of maximum photomultiplier signal. Plots of wavelength vs concentration were obtained separately for chloroform, benzene and cyclohexane and were found to be linear below 50 ppm. Plots of wavelength of maximum reflection vs liquid crystal temperature could also be made to aid in the identification of the trace contaminants.

The technique should be tested with a greater number of contaminants, both individually and in mixtures. It is expected that qualitative and quantitative analysis will require studying complex spectra of the type encountered in spectrophotometry. However, the technique's simplicity and sensitivity may prove a great advantage. Some questions to be answered are, for example, is there a threshold effect in the liquid crystal response and if so at what trace contaminant concentration level? What is the expected lifetime and stability of the liquid crystal response?

3.6 Specific Gas Sensors

A backup system monitoring the major gases and the most important trace contaminants may be desired, no matter how reliable the trace monitoring system becomes. In addition to those techniques mentioned in the previous sections, several

others have been proposed using solid electrolyte or fuel cell concepts (41, 42) or changes in resistance in anion-exchange resins (43). Such specific sensors are usually much lighter and more reliable and sensitive than multi-gas sensors.

Others suggest the application of condensation nuclei counters to detect trace gases, in a time-sharing manner, via their conversion to low vapor pressure liquids or solids (44). For example, ammonia could be detected in .005 ppm concentrations if it were first made to react with HCl, forming particulate NH^4Cl. Furthermore, it must be mentioned that standard analytical procedures, suitably adapted to space use (40) should also eventually be provided in any orbiting or planetary base, as the most reliable research tool.

If research leads to sufficiently sensitive, lightweight and reliable specific gas sensors, we may soon find the use of many sensors preferable to any one complex multi-gas sensor. Certainly failure detection and maintenance problems could be alleviated.

Recommendations for University Research

1. Test and suitably modify standard analytical procedures for use in space.

2. Develop longer lasting, regenerable trace contaminant absorption beds.

3. Develop more sensitive gas chromatographic detectors and evaluate their operation in various g-fields.

4. Develop or improve valves and pumps to increase the

reliability of gas sampling systems at low flow rates and pressures.

5. Study the application of lasers in spectrophotometry.

6. Further investigate the application of Raman spectroscopy.

7. Expand the catalogs of microwave spectra.

8. Develop computer pattern recognition programs to analyze spectra on-line.

9. Continue research with liquid crystals.

10. Propose other innovative monitoring techniques for either specific gases or milti-component gas mixtures.

11. General trade-off studies to determine most reliable and sensitive combination of available techniques.

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IV. BIOLOGICAL MONITORING TECHNIQUES

Since so little is known about the biological environment of an astronaut, it is expected that some type of biological monitoring technique(s) will be provided on future space flights, as soon as flight-qualified instrumentation is available.

In biological monitoring, there are problems associated both with the sampling procedures (1,2,3,4) and with the methods of detection and identification. Monitoring, here, will refer specifically to the detection and identification procedures.

Ideally, a biological monitor should be adaptable to either air or water analysis, provide rapid, automatic and sensitive (tentative allowable concentrations 100 org./ft^3 in air, 10 org./ml. in water) measurements, and also distinguish between microbial species. No single monitoring technique meets all these requirements at the moment, much less those of small size and power penalties. A combination of monitoring techniques will probably be required.

Some of the biological monitoring techniques currently available or proposed, are presented below in arbitrary categories of physical, chemical or biological techniques. Though much research has been done in this area, it suffers from a lack of publications of subsequent results and instrumentation developments. In any case much work remains to be done to develop fully automated, reliable, miniaturized and flight qualified monitoring techniques.

4.1 Physical Techniques

Microbial particles can be detected by light scattering devices or nephelometers in the case of air samples or by Coulter counters in the case of liquid samples (5,9,10,11,12).

Devices have been developed for automated use in spacecraft where the growth of a sample in a liquid or solid culture medium can be detected by the change in its turbidity. They are very sensitive, but several hours are required to detect an initial inoculum of 100 viable organisms; detection would be even slower for lower biological concentrations. Also, since the culture medium cannot be optimal for all types of organisms, detection sensitivity varies with the species involved and may even be absent in certain cases. Identification of the microorganisms is impossible except in terms of the groups of bacteria or viruses which are expected to flourish in the chosen nutrient.

Another approach has been extensively studied where the use of a Coulter counter allows the measurement of specific particle-size concentrations in a sample before and after passing through a liquid nutrient loop (11). This provides a measure of the initial concentration of viable organisms in the sample, but again cannot identify the specific microorganisms involved. The technique was intended for on-line monitoring of a water reclamation system: using nutrient broth, it is believed to be capable of detecting the presence of 1-10 viable organisms/ml within 4 hours. The technique was tested with E. Coli, P. aeruginosa, M. polymorpha, B.

subsilis and X. translucens. Though such an approach could be adapted to air monitoring, it has the disadvantages of

--- required storage of nutrient medium and particle-free water for flushing,

--- inability to identify organisms

--- relatively long delay time before growth of viable organisms is detected

--- reduced reliability due to use of pumps, small orifice tubing, fittings and valves, all susceptible to plugging problems.

A lightweight, low-power light microscope would be a useful tool in the space cabin, especially when scientist-astronauts fly more frequently. Simple designs are available, weighing less than 10 lbs. and requiring only intermittent use of a 6-V. source. It could be used to help in the identification of detected viable organisms or as a periodic check on other monitoring procedures. To be effective, zero-gravity staining procedures should be developed and simplified.

4.2 Chemical Techniques

Adenosine triphosphate (ATP) and flavin mononucleotide (FMN) are present in all living microorganisms so far examined. Therefore, a measure of the total ATP or FMN in a sample is proportional to the total number of living organisms it contains. The approach is implemented by photometrically measuring the light response in the ATP- firefly luciferase bioluminescent reaction or in the FMN - photobacteria luciferase bioluminescent reaction (5,6,7,13,14,15,16). The techniques are very

rapid (light response in a few seconds) and very sensitive (down to 0.1 picogram ATP or 10 micogram FMN), independent of the species involved. However, the number of microorganisms detected depends on the species monitored since, for example, .1 picogram ATP corresponds to 1 protozoan or 10 bacterial cells because of varying ATP (FMN) content with particle size.

The bioluminescent technique is the most promising and most developed of the methods to monitor the total viable biological contaminant population in a sample. A miniaturized fully automatic package of less than 1 cu. ft. is being developed (6,14). However, the method cannot be used to identify microorganisms and one major problem is the expected 6-month life expectancy of the firefly or bacterial luciferase. Bacterial cultures could be carried for enzyme extraction in flight.

A recent chemiluminescent technique uses the reaction of a luminescent chemical (luminol) with cellular extracts (5,6,7). This is similar to the bioluminescent method mentioned above. With the recent development of more stable substrates, the reaction is also rapid (few seconds), accurate, and fairly sensitive ($\sim 10^3$ bacteria). However, the sensitivity is affected by the species involved and the technique also reacts to oxidizing agents and free radicals in the solution, requiring both background and specific reaction measurements to detect only viable organisms.

Fluorescence techniques can be made specific to identifying desired organisms by coupling fluorescent moieties

to selected antibodies and mixing them with microbial samples. The level of contamination can be measured by fluorimetry, comparing the level of fluorescence for specific and non-specific staining. With suitable antibodies, the technique can be used to detect bacteria, viruses or toxins. It is rapid, very sensitive and specific but does not distinguish between viable cells and cellular fragments. Automated devices have been developed for BW surveillance monitors (5,17). The main disadvantages are the preselection of a limited number of organisms to be monitored and storage of appropriate antibody preparations of limited lifetime.

Another method that is specific to identifying micro-organisms measures the phosphorescence of a culture under ultraviolet radiation (18). In contrast to the above techniques it does not require the storage or preparation of any reagents. Also it holds the promise of a technique adaptable to both trace gas and biological monitoring (e.g. using laser & Raman spectra). At a fixed optimal wave-length, the phosphorescence exhibits decay characteristics lasting up to 30 sec., which are specific to the organism in the culture. Only pure cultures have been tested so far, and more development is needed to reach the required sensitivities of at least 10 org./ml or 100 org./ft^3. There remains to determine the sensitivity and identification limits for mixtures of organisms, and whether viable and nonviable organisms can be differentiated. A computer would be required to analyze the complex phosphorescence decay curves.

A gas chromatography method has also been investigated to both detect and identify microorganisms (19,20). It was tested on ether extracts of pure cultures of 29 strains of bacteria. 400 cells/ml of a few bacterial species could be detected after 2-4 hours of growth. The chromatographic peaks of the various volatile compounds were characteristic to the species involved and, like phosphorescence, could be used to differentiate one strain from another. Unfortunately different extract concentrations and column conditions are required to monitor different species. With the electron capture detector, the method could detect down to five picograms of diacetyl and 22 picograms of acetoin. Since these two compounds were present in all the strains tested, and could be detected at such low levels, the authors suggested that monitoring only diacetyl or acetoin might be a very sensitive non-specific method of detecting viable microorganisms. In any case, gas chromatography should be further investigated for its applicability to mixtures of organisms, and to improve its sensitivity and detection speed. It offers the possibility, like phosphorescence, of a hybrid biological/trace gas monitor.

4.3 Biological Techniques:

Methods have been studied to measure biological contamination based on some aspects of microbial metabolism (5,6,7,9,12). Some detect the substrate used by an organism, or the organism itself, by tagging with a known chemical, dye or isotope. For example, enzyme activity can be detected by fluorimetry when phosphate is split from a fluor-phosphate

compound in the growth medium. On the growth of organisms "respiration" can be detected by a Geiger-Mueller tube when $^{14}CO_2$ evolves from a medium containing ^{14}C-labelled carbon sources (e.g. glucose, protein, organic acid...). Such techniques are also useful in research on the mechanism of physiological processes.

Other simpler techniques may measure the pH of a culture medium, observing a sharp decrease with increase in cell numbers. Unfortunately, all these biological techniques require several hours to detect biological growth and are very inaccurate; depending on culture medium, environmental conditions, and the fact that growth does not always begin immediately, erroneous extrapolations to initial biological contamination level are possible. The sensitivities are also still very low ($\sim 10^3$ bacteria).

The most reliable method of detecting viable microorganisms is the standard growth method. It should be included on any mission as a versatile research tool and for spot checks on an automatic monitoring system. The Space Science Board recommends the membrane procedure: if replicate samples on different membranes are exposed to various nutrient media, some biological identification by genus may be possible on the appearance of visible colonies. The species to be detected and therefore the number of available nutrient media would have to be preselected and withstand storage. If a microscope is also provided it could be used to help in the more specific identification of the microorganisms in a culture. The method is very sensitive but requires 24-48

hours incubation of exposed membranes under carefully controlled environmental conditions.

Recommendations for University Research:

1. Develop zero-gravity staining procedures.

2. Simplify and possibly automate standard growth procedures.

3. Test nutrient mediums to determine those that would provide substrates for the rapid growth of a maximum number of biological species.

4. Continue research on phosphorescence techniques.

5. Develop gas chromatographic technique.

6. Propose other innovative monitoring techniques that would provide automatic detection and identification of bacteria, viruses, toxins, etc....

7. Develop techniques to stabilize biological materials such as antibodies, enzymes,... for long-term storage (years).

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