

FINAL REPORT
NASw 871

CONTINUATION OF STUDIES IN
STATISTICAL DECISION THEORY
IN
LARGE SCALE BIOLOGICAL EXPERIMENTS

TO

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"Analysis of the Martian Atmosphere: Its Biological
Significance" by D. Hitchcock and J. E. Lovelock

1.0 INTRODUCTION

This document reports the work carried out in the second phase of the subject project, supported under contract NASw 871, during the contract period covered from May 1, 1965 to July 31, 1966.

Personnel participating in this project are:

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The project was under the technical monitorship of Dr. George Jacobs, Office of Bio Sciences Programs, National Aeronautics & Space Administration, Washington, D.C.

2.0 STUDIES OF BIOTIC ORDER

2.1 Introduction

The first phase of these studies of statistical decision theory for large scale biological experiments was devoted to the problem of defining and interpreting a concept of the value of an experiment which could be employed to aid payload selection decisions for the Mars biological exploration program. This entailed a survey of the mission objectives and experiments proposed for inclusion, with special emphasis on the concept of scientific value of information (with particular emphasis on interrelationships between the results of different experiments and the hypotheses they might jointly tend to confirm or disconfirm) and the likelihood that proposed experiments would yield interpretable or unambiguous results (with particular emphasis on the problem on detectability of machine error and the bias contributed by undetected machine error). This phase of these studies, which was completed in April 1965, resulted in a number of conclusions, among which the most important were that: 1) virtually all biological experiments proposed were designed to demonstrate the existence of a biota in terms of a rather restricted concept of life as bearing a very strong biochemical and functional resemblance to terrestrial life and were such that failure to detect the life form satisfying these restrictive conditions would result simultaneously in failure to increase knowledge of Mars; and 2) these experiments are difficult to implement in that they in general have a great many potential sources of bias due to machine error and such bias is in general more difficult to detect from analysis of the experimental results than is the case for experiments designed to measure the physical and chemical properties of the planet (where such bias is sometimes revealed by the presence of "impossible" results).

Thus, the results of the first phase indicated a need for the following kinds of life detection experiments:

1. Those which employ a more general concept of life and would be capable of detecting life forms which are extremely alien in respect to biochemistry and metabolism.
2. Those which provide useful information even if they fail to demonstrate the existence of a biota.
3. Simple experiments which have a high degree of machine reliability, are easy to monitor for machine malfunction and have a low a priori probability of yielding ambiguous results which are difficult to interpret.

Consequently the focus of this reporting period's studies has been an attempt to find life detection experiments with at least some of these characteristics. The approach taken has consisted of a

2.1 (Continued)

reconsideration of the frequent observation that the fundamental difference between living and non-living matter is that the former are characterized by a high degree of "negative entropy," which has in the past been loosely equated with "information," "order," "structure," "thermodynamic improbability," and "purpose."

This effort has taken the form of examining the empirical implications of the assumption that living organisms are characterized by some feature which can be said, at least on intuitive grounds, to be equivalent to or implied by the negative entropy assumption. (This expedient is dictated by the fact that although the negentropy concept, as for example delineated by Shroedinger*, is an attractive one, it is far from satisfactory theoretically in that it does not yield a rigorous definition of the form in which "order," "information," etc. are to be observed in life processes, and requires an essentially metaphorical use of thermodynamic or information theoretic terms in discussing it.)

Two lines of investigation resulted. The first employed as its departure point the assumption that living organisms are characterized by the ability to establish and maintain a chemical free energy gradient between themselves and some portion of their "non-living" environment and that after death this gradient is gradually dissipated until chemical equilibrium is established. It follows that the observation of a chemical "disequilibrium" (e.g., the existence of a free energy gradient which is anomalous in that it cannot be explained as the steady state consequence of non-biological processes) would constitute evidence of the existence of a biota. The most useful and surprising result of this inquiry was the finding that the terrestrial atmosphere is in such a state of "disequilibrium" and that the existence of terrestrial life could be inferred by, for example, an observing Martian from knowledge of the density and composition of the atmosphere and the solar flux. These results are briefly reported in Section 2.2 below and in the appended draft of a paper entitled "Analysis of the Martian Atmosphere: Its Biological Significance."

The second line of investigation has focused on the concept of biotic order and has consisted in observing the distribution of n-alkanes in a variety of materials of biotic, abiotic, and unknown origin. This has consisted in determining whether the order in these distributions could be measured and whether the amount of measured order is: 1) a monotonically decreasing function of age in material of biotic origin, 2) high for material of biotic origin and low for material of abiotic origin, and 3) whether such a measure provided any insight into the possible origin of material of unknown (meteoritic) origin. These results are reported in Section 2.3.

2.2 Biological Significance of Atmospheric Compositions and Surface-Atmosphere Reactions

This portion of the studies conducted during this reporting period concentrated on demonstrating the validity of a characterization of life in terms of its ability to establish and maintain a free energy gradient between itself and some portion of its environment. The existence of such a gradient should result in two things: a disturbance of the nominally "non-living" portion of the environment so severe as to be recognizably not attributable to the uncontrolled action of abiological mechanisms, and the direct observation of the existence of the physical or chemical gradient itself. If this assumption provides a valid basis for the design of Martian life-detection experiments, then it should also be true of earth; specifically, it should be possible to determine from an examination of physical or chemical properties of Earth that life exists here, and this should be possible without any assumptions regarding the detailed chemical or physical nature of the biota.

The results of this portion of the study are contained in the appended draft of a paper entitled "Analysis of the Martian Atmosphere: Its Biological Significance." (This paper has not yet been accepted for publication, and may undergo some minor modifications.)

The extrapolation of these results to the question of the possible validity of a Martian atmospheric life-detection experiment are further considered in Section 3 of this report.

2.3 Biotic Structure in N-Alkane Distributions

2.3.1 Order Measures in Gas Chromatography

It has been frequently noted that the concentrations of n-alkanes in biotic materials, such as oil crudes, shale residues, etc., tend to exhibit characteristic ordering, in that the n-alkanes of odd carbon chain length are present in greater abundance than the penultimate and successor even numbered homologs. Indices based on this so-called odd/even preference have, in fact, been constructed and used as measures of the suitability of crude oil stocks for economic exploitation.

During the first year of the current project, Professor J. E. Lovelock at the University of Houston drew the attention of project personnel to the fact that this characteristic of gas chromatograms of n-alkanes derived from biotic material appeared capable of further generalization. Specifically, Dr. Lovelock showed that the relative concentrations of n-alkanes in the products of a Fisher-Tropsch hydrocarbon synthesis (which has been reacted to near equilibrium) are closely approximated by a classical Poisson distribution, while materials of biotic

2.3.1 (Continued)

origin deviate to a greater or lesser extent from this distribution. The root mean square deviation of the observed concentration from those predicted by a Poisson distribution of best fit appeared to be roughly inversely related to the age of the material from whence the sample is derived, i.e., old biotic materials tended to fit a Poisson better than recent biological materials.

Quantities measuring the degree of order/disorder in a sample of material of putative biological origin could be of considerable potential use in tracing the history of the sample and classifying it as to origin. Since the Poisson distribution is a single parameter function, it is clear that it could only serve to measure one type of departure from randomness. A semi-empirical study was, therefore, initiated with the cooperation of personnel at the University of Houston to attempt to develop more general measures of order in gas chromatograms.

2.3.2 Life As An Order Conserving Process

It has been frequently observed that living systems and their immediate surroundings constitute regions of space in which the second law of thermodynamics is held in abeyance for significant periods of time. From this viewpoint, we regard the presence of a living system as embodying a set of constraints on the number and kinds of physio-chemical interactions which can occur in the immediate region of the organism. This system of reaction constraints is thus reflected by greater order in the array of substances in the vicinity of the organism, and this greater order is reflected as a lower entropy of organization relative to that which would obtain if the constraints were not present. After death the entropy of the system increases at a rate determined by local conditions until eventually the matter once comprising the system ceases to have relatively low entropy.

Consider a surface or region of a planet at constant temperature T and pressure P . Let the surface contain K chemical species S_1, S_2, \dots, S_k and let the chemical potential of the i^{th} species be M_i . As time passes, the various species will undergo interaction leading to the synthesis of additional substances and the degradation of others. After the passage of a period of time, which may be very long, the system will approach equilibrium in the sense that no further detectable changes in concentration will be noted with time. Suppose now that a sample of this mixture is analyzed and the relative concentrations of the various species determined. There will result the distribution of concentrations of the various products in the sample. The distribution of concentrations will be constrained by the free energies of formation of the equilibrium mixture. In principle, the concentrations of the species in the equilibrium mixture are predictable from knowledge of the starting composition and the free energies of formation of the various products of reaction.

2.3.2 (Continued)

In general, any physio-chemical system will, according to the second law of thermodynamics, tend to approach a state of minimum free energy or maximum entropy. Living systems, on the other hand, contravene this tendency for periods of time equal to some multiple of the life span of the system. In consequence, the chemical composition of a region occupied by a living system will not reflect a mixture of products resulting from an unrestricted sequence of physio-chemical interactions. The spectrum of possible reactions is constrained and certain products will not be present in the reaction mixture. As a result of this constraint the free energy content of the system is greater and the entropy less the equilibrium value. Such constraints are reflected in the presence of what will be termed "biotic order" in the distribution.

2.3.3 Objective of Program

The basic objective of the work described in this section was to determine whether or not it is possible to construct a measure or measures which could be computed from a digitized gas chromatogram which would serve to characterize the degree of order or disorder in the distribution of the relative abundances of the n-alkanes in a sample of matter.

In the context of this objective, we shall refer to the results of a highly directed chemical process as yielding a sample of matter which is organized or ordered. For example, when a chemist carries out the synthesis of a specific alkane from a specific starting material, he generally arranges conditions so that substantially only the desired compound is present in the final products of the reaction with minimal contamination by other substances. Such a sample is highly ordered since only the desired substance is preponderately contained in the reaction product.

Ideally, the proposed measures should satisfy the following general criteria:

1. It should range from some minimum for a totally unordered sample to a maximum value for an ordered one.
2. The magnitude of the measure should be a monotonic function of the degree of degradation of a sample: degradation of an ordered sample should lead to a diminution of the measure.
3. The measure should be additive in that if a highly ordered sample is mixed with a low ordered sample, the resulting measure should correspond to the average of the measures of each sample separately.

2.3.4 Temperature Programmed Gas Chromatography

The experimental data utilized in this report were obtained by means of temperature programmed gas chromatography. Figure 1 depicts a simplified version of this system, which consists essentially of a) a temperature controlled oven, b) a check valve system for the impulsive injection of the sample into the carrier gas stream, c) the chromatogram column, and d) the detector system. The sample is placed in the oven and subjected to a temperature regimen, which may range from mild volatilization for a period of some hours, to outright pyrolysis of the material. As each species contained in vapor is adsorbed and eluted from the column, its presence in the column effluent is detected and recorded on the moving strip chart. The time of elution is the prime identifying variate since, in a homologous series, the time of elution or retention time on the column is proportional to the molecular weight of the species in question. Each species as eluted generates an essentially Gaussian curve on the strip chart record, the area under the curve being essentially proportional to the relative concentration of the given species in the sample injected on the column.

In a well-controlled chromatogram, the widths of the peaks at the base are essentially constant so that for the purpose of obtaining estimates of relative concentrations it is sufficient to measure the peak heights. Division of each peak height by the sum of all the peaks in the chromatogram yields an estimate of the relative concentration of each species in the original mixture. This estimate is, however, a biased one, since at room temperature all n-alkanes of chain length of $C = 8$ or less are lost from the sample due to their volatility.

Temperature programmed chromatography utilizing a variety or regimens was employed in this project. The resulting chromatograms were digitized by measurement of peak heights from the variable base lines of the chromatograms to obtain the distribution of relative concentrations of n-alkanes in the starting mixture.

2.3.5 Characterization of Order In a Chromatogram

A digitized chromatogram of a sample of n-alkanes obtained in the foregoing manner is a sequence of numbers ordered by the number of carbons in the chain. The question arises as to what underlying law or process could give rise to the observed sequence. There are, in fact, an infinite number of possible laws to choose from and no finite body of data will allow one of these to be selected as the true one. In general, we must be content with the selection of a rather crude and simplified approximation of the underlying law or process. For the purposes of this project, we have selected a class of processes which can be described essentially in terms of the information which some subset of the ordinates of the observed chromatogram conveys about the whole chromatogram.

2.3.5 (Continued)

When a Fisher Tropsch alkane synthesis, for example, is performed and allowed to come to equilibrium and the product mixture is chromatographed, a chromatogram such as the one shown in Figure 2 is obtained. Figure 3 is the digitized version of the chromatogram, in which the n-alkane peak heights in Figure 2 are represented by the heights of the bars of the histogram. The salient feature of the histogram in Figure 3 is the smooth unimodal appearance of the envelope. This smooth, roughly symmetric appearance of the histogram is fairly typical of those resulting from samples of "old" biological materials or from recent biotic materials subject to thermal degradation or from simple multiproduct synthesis which have been permitted to reach equilibrium.

In contrast to the general visual appearance of chromatograms of old or degraded biotic samples is the type of chromatogram obtained with samples of recent biotic origin and exemplified by the one in Figure 4, which is a sample of n-alkanes obtained from bat guano approximately 5×10^3 years old. In this chromatogram, there does not appear to be a preferred or most abundant concentration with the concentration of all other species more or less predictably related to it, as there was in the products of the Fisher Tropsch synthesis.

In addition to this lack of smoothness the chromatogram of the sample of bat guano manifests the characteristic tendency of biotic materials to preferential odd/even concentrations of n-alkanes.

The measures used in this project to characterize the order in a gas chromatogram is based on the following ideas: consider two contrasting dummy chromatograms, as shown in Figure 5, curves A and B, and tabulated in Table I.

TABLE I - TWO DUMMY CHROMATOGRAMS

Carbon No.	A	Y_i	\hat{S}_i	B	\hat{Y}_i	δ_i
16	0	-	-	14	-	-
17	36	32	4	99	52	47
18	64	60	4	89	72	17
19	84	80	4	46	47	-1
20	96	92	4	5	34	-29
21	100	96	4	23	37	-14
22	96	92	4	23	37	-14
23	84	-	-	69	-	-

Visually, one of the salient differences between the two sequences is that chromatogram A is relatively smooth and predictable in appearance while B is quite the opposite. This is not at all surprising when we realize that series A is actually the ordinates

2.3.5 (Continued)

of $Y = 40C - 4C^2$, while series B is a sequence of random digits in the range 0 - 99.

Suppose that series A was presented to an observer with some one value other than the first or last deleted, e.g., one value is removed and a space left in the record. Now suppose we asked the observer to use any methods he cares to form his best estimate of the deleted value. It is clear that from inspection of the record that the observer is likely to form a reasonably close guess at the value. Let Y_i denote any deleted ordinate and suppose the observer elects to utilize a linear interpolation in order to construct his estimate \hat{Y}_i of Y_i . Thus:

$$\hat{Y}_i = [Y_{i+1} + Y_{i-1}] / 2 \quad (1)$$

Thus, for A the value of $Y_4 = 84$ and $\hat{Y}_4 = [Y_5 + Y_3] / 2 = [96 + 64] / 2 = 80$

Suppose the observer applies this interpolation process to each ordinate and the failure of the interpolation function to give the correct value Y_i is estimated by the discrepancy:

$$\delta_i = Y_i - \hat{Y}_i \quad (2)$$

These quantities are tabulated in Table I. In the case of chromatogram A, there is a constant discrepancy of 4 for all "carbon values," but it is readily seen that the interpolation procedure gives very good estimates of the values of Y_i . In fact, since the discrepancy is a constant =4 this value could be included in the interpolation to give the exact value of Y_i . In chromatogram B, on the other hand, use of the same interpolation function gives a very poor prediction of the actual values of the function as evidenced by the larger and irregular behavior of the δ_i .

In general for "smooth" well-behaved functions such as the one in Column A of Table I, there is a high degree of predictability about any particular ordinate, and an observer is able to supply rather close estimates of any one missing value on the basis of the remaining data. For more irregular, more random functions, such predictability is not present.

From the information theoretic viewpoint, ordinates from sequences exemplified by chromatogram A may be characterized as having a very low information content whereas sequences such as B have a relatively high information content. Thus, in spite of its being composed from a random number table, series B exhibits the characteristic we equate with biotic order. This somewhat counter-intuitive statement

2.3.5 (Continued)

can be explained as follows: in chromatogram A, when the observer has formed his estimate and is then allowed to see the actual value he finds that the observed and actual values are almost the same. Therefore, knowledge of the actual value contributes very little additional information to the observer since he is able to closely estimate it prior to actually seeing it. In chromatogram B the various values are essentially unpredictable since they came from a table of random digits. Since the predicted value is completely unrelated to the actual value, knowledge of the value conveys a large amount of information to the observer since the best prediction he can make prior to seeing it is that the value lies between 0 and 99.

This notion of the "reconstructability" of a chromatogram is in complete qualitative accord with conventional information theory and suggests that the measurement of the degree of order in a chromatogram might be accomplished by use of simple interpolation methods.

2.3.6 Use of Interpolation Methods

Let the ordinates of a given digitized chromatogram be denoted by $Y_1, Y_2, Y_3 \dots Y_i \dots Y_T$.

Suppose for $i = 2 \dots T-1$ we compute:

$${}_2\hat{Y}_i = [Y_{i+1} + Y_{i-1}] / 2 \quad (3)$$

$$\text{and } D_{2i} = Y_i - {}_2\hat{Y}_i \quad (4)$$

and for $i = 3 \dots T-2$ we compute

$${}_4\hat{Y}_i = [Y_{i+2} + Y_{i-2}] / 2 \quad (5)$$

$$D_{4i} = Y_i - {}_4\hat{Y}_i \quad (6)$$

The quantities D_{2i} and D_{4i} will measure respectively the predictive value of the result of an interpolating operator, operating on ordinates on each side of a deleted value and on ordinates once removed from a deleted value.

The behavior the quantities D_{2i} and D_{4i} as functions of the underlying behavior of the chromatogram must now be examined.

Given a series of ordinates $Y_1, Y_2 \dots Y_T$, the mean value of the sequence is defined as:

$$\bar{Y} = \frac{1}{T} \sum_{i=1}^T Y_i \quad (7)$$

2.3.5 (Continued)

and its variance $V(y)$ as:

$$V(y) = \frac{1}{T} \sum_{i=1}^T (y_i - \bar{y})^2 \quad (8)$$

The sequence Y_1, Y_2, \dots, Y_T can, according to Fourier's theorem be expanded into the series:

$$y_i = \sum_{N=-\infty}^{\infty} C_N \exp(jn\pi i/T) \quad (9)$$

$j = \sqrt{-1}$

The terms $(jn\pi i/T)$ are completely known for any value of T since they can be looked up in a table. Thus, all sequences of length T have the same set of functions, $\exp(jn\pi i/T)$. What distinguishes one sequence from another is the sequence of co-efficients C_n which are definite numbers which differ for different series. A plot of the quantity $|C_n|^2$ against $n\pi/T$ is in fact the power spectrum of the sequence Y_1, Y_2, \dots, Y_T and different sequences each of length T will have different power spectra.

It is easy to show that:

$$V(y) = 1/2 \sum_{n=-\infty}^{\infty} |C_n|^2 \quad (10)$$

and since $V(y)$ measures the total variation of the sequence, equation (10) relates this total variation to the power spectral components C_n^2 . Thus equation (10) shows that the total variation of the original sequence depends on the magnitudes of the co-efficients C_n , and thus on the spectral components, $|C_n|^2$.

The problem of estimating the values of the C_n from a given observed sequence of values Y_i is a problem in spectral analysis. A number of methods and procedures are known which will provide estimates of the C_n . The quality of these estimates, as might be expected, however, depends on the length of the sequence available. Since the lengths available in the current work are very short (30 points or less) the estimates used are relatively crude.

Digital filtering based on the interpolation formulas described above was used to obtain these broad estimates of the C_n . This method is based on the following considerations:

The quantity $D_{2i} = y_i - 2\hat{y}_i$ (11)

may, by substitution of $2\hat{y}_i = [y_{i+1} + y_{i-1}]/2$ into equation (11) be written as:

$$D_{2i} = y_i - (y_{i+1} + y_{i-1})/2 \quad (12)$$

2.3.5 (Continued)

Defining the shift operators:

$$\begin{aligned} E Y_i &= Y_{i+1} \\ E^{-1} Y_i &= Y_{i-1} \end{aligned} \tag{13}$$

we have:

$$\begin{aligned} D_{2i} &= (Y_i - 1/2 E Y_i - 1/2 E^{-1} Y_i) \\ &= 1 - (E + E^{-1}) Y_i / 2 \end{aligned} \tag{12a}$$

Since

$$\begin{aligned} E &= \exp j\theta \\ E^{-1} &= \exp -j\theta \end{aligned}$$

we have:

$$D_{2i} = (1 - \cos\theta) = 2 \sin^2 \theta / 2 \tag{14}$$

The quantity D_{2i} may be regarded as the result of passing the sequence Y_i through a filter with transfer operator of $2 \sin^2 \theta / 2$. Substituting the value of D_{2i} in equation (14) into equation (9) yields:

$$D_{2i} = 2 \sum \sin^2(n\pi/2T) C_n \exp(jn\pi i/T)$$

which represents a new sequence resulting from the passage of Y_i through the filter defined by equation (12a).

The time variation of D_{2i} is given by the variance of the D_{2i} , namely:

$$V(D_{2i}) = 2 \sum |C_n|^2 \sin^4(n\pi/2T) \tag{15}$$

The factor $\sin^4 n\pi/2T$ is shown in Figure 2 and tabulated in Table 2.

TABLE 2	$\sin^4(n\pi/2T)$	and $\sin^4(n\pi/T)$
n	$\sin^4 \theta/2$	$\sin^4 \theta$
0	0	0
1	.0045	.0625
2	.0625	.5623
3	.2500	1.000
4	.5623	.5623
5	.9329	.0625
6	1.000	0

2.3.5 (Continued)

The variance ratio $V(D_2) / V(Y)$ is thus a measure of the magnitude of the contribution being made to the original sequence $Y_1, Y_2 \dots Y_T$ by high frequency components in the original sequence. This is seen by considering one frequency component, $C_n \exp(j n \pi / T)$, in the original sequence defined by equation (9). The contribution of this component to the variance of the original sequence is $|C_n|^2 / 2$. After the original sequence has passed through the interpolating filter the result is D_{2i} with variance $V(D_2)$. The contribution of the selected component to $V(D_2)$ is:

$$2 |C_n|^2 \sin^4(n \pi / 2T) = 2 |C_n|^2 \sin^4 \theta / 2$$

Now, if n is small θ is small and the factor $\sin^4(n \pi / 2T)$ is small. Hence even if $|C_n|^2$ is large the filter factor picked up by passage through the filter will suppress it so that the component will make no contribution to $V(D_2)$. Thus, if the original sequence is dominated by C_1, C_2 and C_3 these terms will be suppressed by the filter and $V(D_2)$ will be much smaller than $V(Y)$. On the other hand, if C_4, C_5 and C_6 dominate, the filter factor will not greatly suppress them and the contribution of these components to the filter output will be substantially the same as their contribution to the original sequence. Then $V(D_2)$ will be approximately the same as $V(Y)$.

The filter defined by the interpolation function:

$$D_{4i} = Y_i - 1/2(Y_{i+2} + Y_{i-2}) \quad (16)$$

is representable in an analogous way by:

$$D_{4i} = 2 \sin^2(n \pi / T) Y_i \quad (17)$$

with $V(D_4) = 4 \sin^4(n \pi / T) C_n^2 \quad (18)$

This factor is also tabulated in Table 2 and plotted in Figure 6. As can be seen this factor tends to suppress low and high frequencies and detect frequencies in the range of 1/4 cycles. As a consequence the ratio:

$$V(D_4) / V(Y)$$

is a measure of the amount of middle frequency activity in the original sequence Y_i .

The foregoing argument may be illustrated by a digitized chromatogram of a petrochemical refinery wax, obtained from the Shell Oil Company and containing some 100 hydrocarbons, admixed with 5% Spanish moss.

2.3.5 (Continued)

TABLE 3 DIGITIZED CHROMATOGRAM OF N-ALKANES FROM SHELL WAX PLUS 5% SPANISH MOSS

Carbon No.	Y_i	\hat{Y}_i	$D_{2i} = Y_i - \hat{Y}_i$
20	1.8	-	-
21	17.0	29.4	-12.4
22	57.0	68.8	-11.8
23	120.6	106.2	14.4
24	155.4	139.3	16.1
25	158.0	144.0	14.0
26	132.7	133.0	-0.3
27	108.0	97.8	10.2
28	63.0	75.5	-12.5
29	43.0	42.0	1.0
30	21.0	32.0	-11.0
31	21.0	-	-

$V(Y) = 2991$

$V(D_2) = 133.2$

$|C_1|^2 = 5658$

$|C_2|^2 = 272$

$|C_3|^2 = 8$

$|C_4|^2 = 0$

$|C_5|^2 = 4$

$|C_6|^2 = 37$

The large value of the co-efficient $|C_1|^2 = 5658$ indicates that the chromatogram is dominated by a sine term with a basic frequency of 1/2 of a cycle over the record.

Now, the ratio

$$J_1 = V(D_2)/V(Y) = 0.044$$

reflects the fact that higher frequency components are absent from the spectrum while the ratio:

$$J_2 = V(D_4)/V(Y) = 0.344$$

(nearly ten times the value of J_1) arises from the dominating role of C_1 and C_2 in the chromatogram.

2.3.5 (Continued)

For the purposes of analysis it is appropriate to examine the behavior of the logarithms of J_1 and J_2 rather than the ratios themselves since the variance of the logarithm of a ratio of variances is the reciprocal of the number of points in the chromatogram diminished by 2. Thus, the quantities:

$$K_1 = 10 \log J_1$$

$$K_2 = 10 \log J_2$$

$$Z = K_1 - K_2$$

which express the spectral estimates on the decibel scale, will be of roughly equal variability since the chromatograms are of approximately the same length.

In this example:

$$K_1 = -13.47$$

$$K_2 = -5.27$$

$$Z = -8.20$$

In summary to this point, the total variation of a sequence Y_i is representable by its variance $V(Y)$ which in turn can be represented as one-half the sum of squares of the co-efficients C_n in the Fourier series expansion of the original sequence. Application of the digital filter:

$$F_2 = 1 - 1/2(E + E^{-1})$$

yields a new sequence D_{2i} whose time variation $V(D_2)$ will tend to be large if the original series contains higher frequency components and small if the sequence is smooth and "well behaved." The ratio $J_1 = V(D_2)/V(Y)$ will measure the relative contribution of these higher frequency components to the original sequence.

Similarly the filter:

$$F_4 = 1 - 1/2(E^2 + E^{-2})$$

will yield a variance $V(D_4)$ which is large if the sequence is smooth and small if it approaches a constant.

For the purpose of tabulating the results of the experimental work the two quantities:

$$K_1 = 10 \log J_1$$

$$K_2 = 10 \log J_2$$

$$Z = K_1 - K_2$$

2.3.5 (Continued)

which represent the ratios on the decibel scale have been chosen as the quantities at prime interest.

2.3.6 Results

Digitized versions of experimental chromatograms obtained by Dr. Peter Simmonds at the University of Houston are the basis of the results presented here. Three primary questions were studied. These were:

1. The relationship of the proposed measures to the age of samples of biological materials;
2. The way in which the measures behaved under thermal degradation of biotic materials;
3. The behavior of the measures as a function of biotic admixture.

2.3.7 Behavior of Measures as Function of Age

In Table 4 several samples of biotic material of differing ages are tabulated together with the quantities K_1 and K_2 computed from the digitized n-alkane gas chromatograms obtained from them. In Figure 7 the quantity $Z = K_1 - K_2$ is plotted against the logarithm of the age of the sample and the conventional least squares line $Z = a + b \log t$ fitted to the ten points.

TABLE 4 ORDER MEASURES COMPUTED ON BIOTIC MATERIALS
OF SEVERAL AGES & NATURE

Sample	Age (Years)	J_1	J_2	$Z=J_1-J_2$
Gun Flint Chert Alkanes	1×10^9	-8.30	-2.23	-6.07
" " " "	1×10^9	-8.21	0.53	-8.74
Precambrian Crude Oil	1×10^9	-22.22	-16.00	-6.22
Cambrian Crude Oil	5×10^8	-14.56	-11.55	-3.01
Bituminous Coal	2.5×10^8	-1.15	-5.23	4.08
Cretaceous Oil Crude	6.5×10^7	-17.70	-12.50	-5.20
Eocene Oil Crude	3.6×10^7	-0.46	-8.96	8.50
Bat Guano	5×10^3	3.58	-10.61	14.19
Sheep's Wool Wax	1×10^0	-0.30	-7.24	6.94
WaxLigustrum	1×10^0	3.01	1.79	1.22
Cow Manure	1×10^0	4.13	-1.66	5.79

2.3.7 (Continued)

In Table 5 the analysis of variance of regression for these data is exhibited.

TABLE 5 ANALYSIS OF VARIANCE OF REGRESSION

Nature of Variation	Degrees of Freedom	Mean Square
Regression	1	183.66*
Residual	9	40.64

* Significant at $p = 0.07$ level

$$a = 7.27$$

$$b = -1.08 \pm 0.50$$

$$s = 6.4$$

The slope, $b = -1.08$ is significantly different from zero ($p = 0.07$) and the measure Z appears to decline by 1.08 db per 10 fold change in age. Clearly additional data are needed, especially in the range of 10^2 to 10^7 years, in order to substantiate the precise shape of the function relating age to loss of structure.

In general, linearity of the measure with logarithm of time is not to be expected because:

1. There is appreciable error in the dating of the older materials;
2. The different materials probably differed in their intrinsic order at the time of origin;
3. The rate of loss of order is undoubtedly affected by different local conditions of temperature and pressure prevailing at the site.

2.3.8 Thermal Degradation of Biologic Materials

Exposure of biogenic mixtures of n-alkanes to elevated temperatures should accelerate the approach to equilibrium and thus should be detectable as a loss of structure or order with increasing time of exposure. To test this hypothesis, samples of Spanish moss were exposed to various regimens of time and temperature at (essentially) constant total pressure. Table 6 exhibits the results obtained.

2.3.8 (Continued)

TABLE 6 EXPOSURE OF SAMPLES OF SPANISH MOSS TO TEMPERATURE REGIMES

Temperature °C	Duration of Exposure (hours)	K ₁	K ₂	K ₁ -K ₂
25	(Control)	6.00	-6.99	12.99
350	24	2.83	-5.62	8.45
350	48	2.79	-5.62	8.41
350	96	-9.51	-11.39	2.88
350	116	-3.51	-12.08	8.57
350	164	-12.52	-11.55	-0.97
25	(Control)	3.75	-10.36	14.11
300	24)	3.78	-9.87	13.65
325	48)			
375	16	3.52	-7.67	11.19

In Figure 8 the isothermal series at 350°C. for periods of exposure up to 116 hours are presented together with the least squares regression line. In Table 7, the analysis of regression variance is shown.

TABLE 7 ANALYSIS OF REGRESSION VARIANCE OF ISOTHERMAL DEGRADATION SERIES

Nature of Variation	d. f.	Mean Square
Regression	1	88.9*
Residual	4	8.4

*Significant at $p = 0.05$

$$a = 11.77$$

$$B = -0.068 \pm 0.021$$

$$s = \pm 2.9$$

The significant negative slope in Table 7 indicates that exposure to 350°C. leads to a loss of order of 0.068 ± 0.021 db per hour of exposure.

On the basis of the results in Table 7 it would appear that degradation proceeds at an appreciable rate only above some critical temperature about 325°C., since the sample heated for 24 hours at 300°C. and then for a further 48 hours at 325°C. shows negligible degradation.

The sample held at 375°C., on the other hand, suffered a loss of 0.018 db per hour, which is not significantly different from the isothermal rate. The extremely small sample size available limited these comparisons to nothing more than a suggestion. Further and much more extensive data would be of interest.

2.3.9 Comparison of Quasi-Abiogenic and Biogenic Materials

In Table 8 the measures computed on several classes of materials have been assembled. Group I, consists of materials of indubitable biologic origin such as wool, wax, cow manure, etc., some of which are repeated from Table 4. The second group consists of the results from several Fischer Tropsch hydrocarbon syntheses run to apparent equilibrium, a sample of refinery wax, and, included for reference, the measures computed for a Poisson distribution. The third group are of meteoric origin together with a sample of laboratory dust.

TABLE 8 THREE CLASSES OF MATERIAL

Group	Sample	K_1	K_2	K_1-K_2
I	Cow Manure	4.13	-1.66	5.79
	Bat Guano	3.58	-10.61	14.19
	Spanish Moss	3.75	-10.36	14.11
	Wool Wax	2.79	-4.44	7.23
	Wax Ligustrum	3.01	1.79	1.22
II	Wax (Shell Oil)	-16.00	-4.78	-11.22
	Fisher Tropsch	-15.23	-8.06	-7.17
	" "	-16.02	-5.37	-10.65
	" "	-22.22	-22.22	0
	Poisson	-17.96	-18.54	0.58
III	Orgeil #1	-1.57	-0.06	-1.37
	Orgeil #2	-8.00	-3.11	-4.89
	Murray II	-12.80	-5.26	-7.54
	Lab Dust	-14.03	-9.27	-4.76

Although the products of a Fisher Tropsch synthesis cannot be regarded as abiogenic, it would appear to be reasonable to regard such a synthesis as a model of the types of processes occurring in an equilibrium, unconstrained system.

If this view is accepted then the small sampling in Table 8 would suggest that, in general, for biotic materials the measure $Z=K_1-K_2$ is positive.

The products of the Fisher Tropsch reaction are zero or negative while the Poisson distribution gives a small positive value.

The general result is that biotic organized materials can be distinguished from abiotic materials by the positive values of their Z measures.

If this basis of discrimination is valid, then it would appear that the meteoric samples lie in an intermediate position and might be classified as essentially unorganized or alternatively as being very old. The latter arises from consideration of the fact that the meteoric Z values approximate those of ancient oils aged about 10^9 years.

2.3.10 Additivity of Measure

Under the assumption that the measure Z characterizes the degree of organization in a sample, it follows that chromatograms derived from mixtures of biotic and abiotic materials should yield numerical value of Z, which are functions of the amount of biogenic material in the sample. To examine this point, samples of refinery wax (Shell Oil Co.), previously shown to yield large negative values of Z, were mixed with samples of Spanish moss (which consistently yield positive Z values) and the results chromatographed. Table 9 shows the results obtained.

TABLE 9 RESULTS FROM MIXTURES OF WAX AND SPANISH MOSS

Material	K ₁	K ₂	K ₁ -K ₂
Wax	-14.95	-6.07	-7.88
Spanish Moss	5.39	-10.81	16.20
Wax + SM 0.1%	-14.32	-5.33	-8.99
" " 0.3%	-14.90	-6.97	-7.93
" " 0.5%	-13.76	-5.37	-8.39
" " 0.7%	-14.94	-6.78	-8.16
" " 1.0%	-13.77	-4.42	-9.35
" " 3.0%	-13.10	-4.20	-8.90
" " 5.0%	-13.47	-5.27	-8.20
" " 7.0%	-12.45	-6.50	-5.95
" " 10%	-11.60	-5.14	-6.46

In Figure 9 these data have been plotted together with the least squares line. The analysis of regression variance is exhibited in Table 10.

TABLE 10 ANALYSIS OF REGRESSION VARIANCE FOR DATA IN TABLE 9

Nature of Variation	Degrees of Freedom	Mean Square
Regression	1	5.20*
Residual	8	0.63

*Significant at p = 0.05 level

$$\begin{aligned}
 a &= -8.64 \\
 b &= +0.218 \pm 0.076 \\
 s &= \pm 0.80
 \end{aligned}$$

The significantly positive slope suggests that in the range of values used here a 1% addition of Spanish moss to this wax confers 0.218 db of organization on the paraffin wax sample.

2.4 Discussion

In this section the results have been presented of a study in which the amount of order in gas chromatograms of the n-alkanes contained in a variety of materials have been measured in terms of a quantity, Z, which essentially detects the frequency range required to specify the form of a given chromatogram. This quantity is generally positive with an average of 5.0 for recent biogenic materials such as sheeps wool, Spanish moss, wax legustrum, etc. For ancient materials of biotic origin, for samples of hydrocarbon mixtures taken from reactions permitted to reach equilibrium, for materials of meteoric origin, and for at least one contemporary material subjected to thermal degradation, the chosen measure becomes distinctly negative.

Although the three regression relationships presented in Figures 7, 8 and 9 appear to be significant, they are all obviously perturbed by a great deal of statistical variation. Unfortunately, this wide variation is at least in part due to a well known consequence of all aspects of attempting to estimate spectral components from finite stretches of data. A type of uncertainty principle holds in which:

Resolution x precision = a constant proportional to number of data points,

e.g., for a record of give length the more precisely we attempt to estimate the spectral components the less the resolution which can be obtained. It is for this reason that only two very broad estimates have been used in this study. Nevertheless, the data collected to date would indicate that these spectral components can be usefully implemented to discriminate biotic from non-biotic materials. One interesting application, for example, could be made of the relationship in Figure 7 in which loss of structure with age and sample has been portrayed. If additional data could be obtained to establish this relationship with a high degree of certainty, then it would be possible to extrapolate the given data points back to zero time and thus obtain estimates of the level of organization which prevailed at the time of the materials. Another useful application is the use of data such as those portrayed in Figure 9 in which abiotic materials contaminated with residual biotic substances may be discriminated as to degree of contamination.

The question may be asked why the foregoing analyses were not carried out in terms of the more conventional types of spectral analysis and the answer is very simply that the very restricted number of data points available with any given chromatogram precluded the effective use of such procedures. There is, however, no doubt that the filters and the estimation procedures used in this work can be considerably "sharpened," and this sharpening together with adequate replication of the experiments should improve the precision of the resulting estimates.

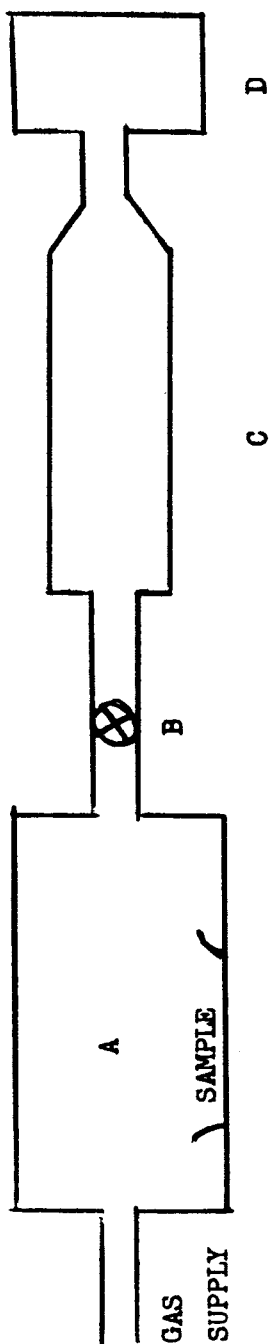


FIGURE 1. TEMPERATURE PROGRAMMED.
GAS CHROMATOGRAM

55° - 325°C AT 7 1/2°/MIN
CHART SPEED 12" / HR

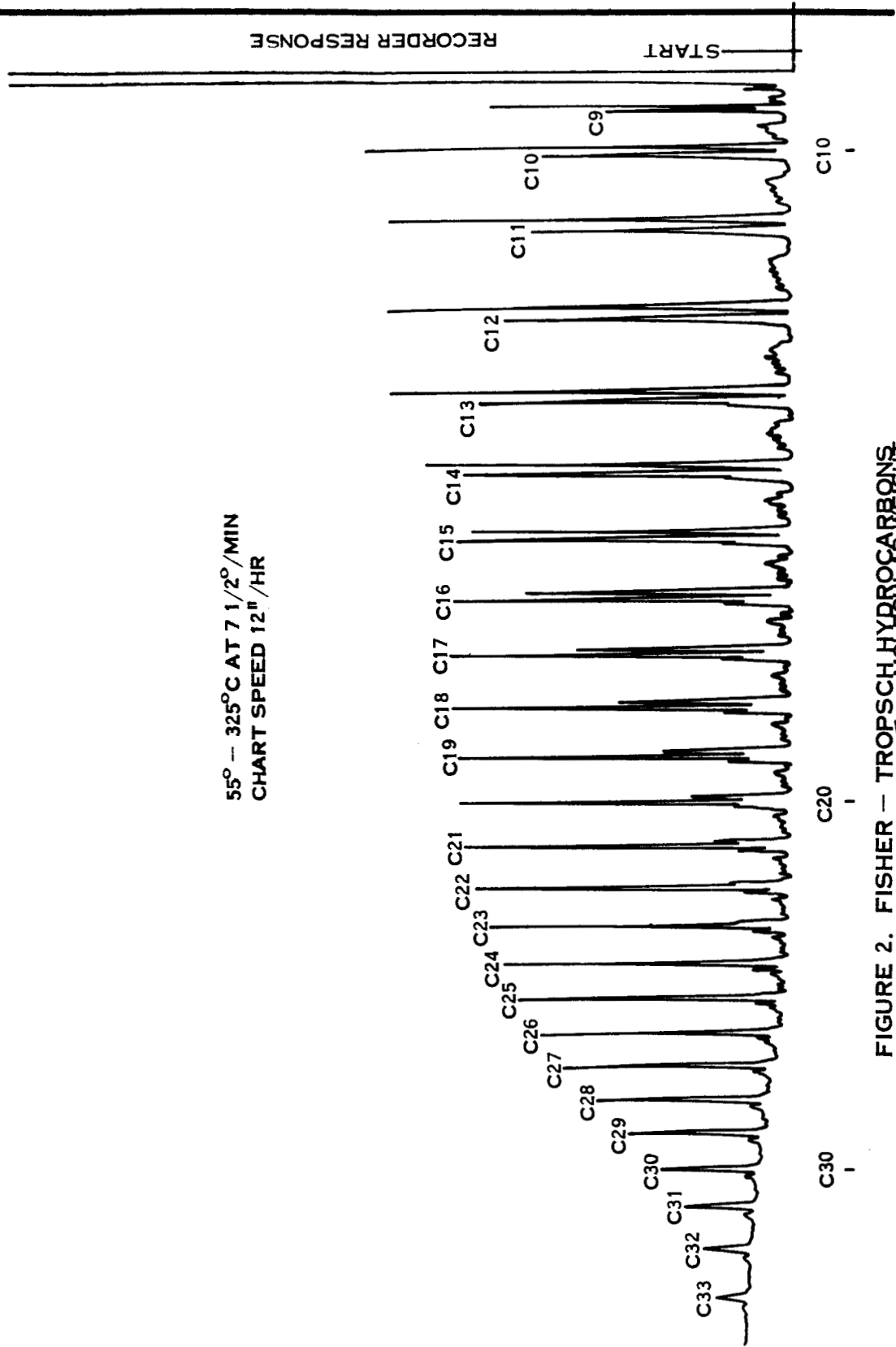


FIGURE 2. FISHER - TROPSCHE MOLECULAR WEIGHT

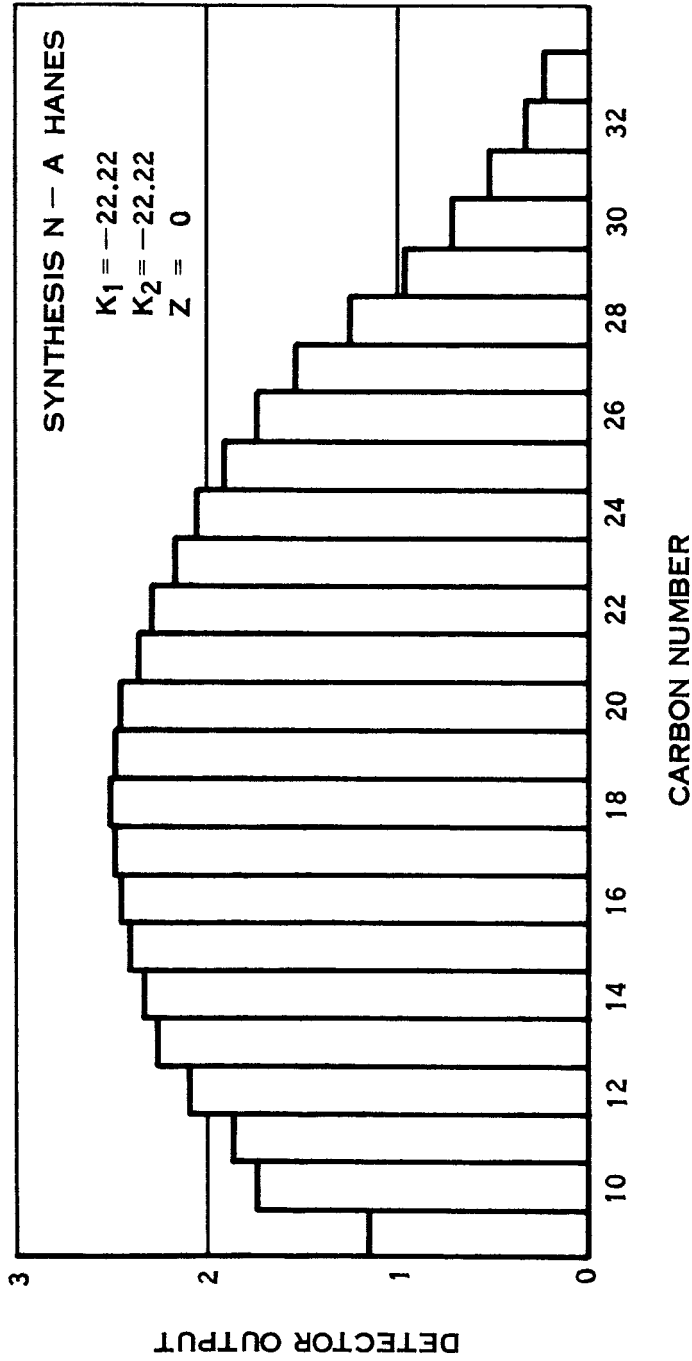


FIGURE 3. FISHER TROPSCH EQUILIBRIUM

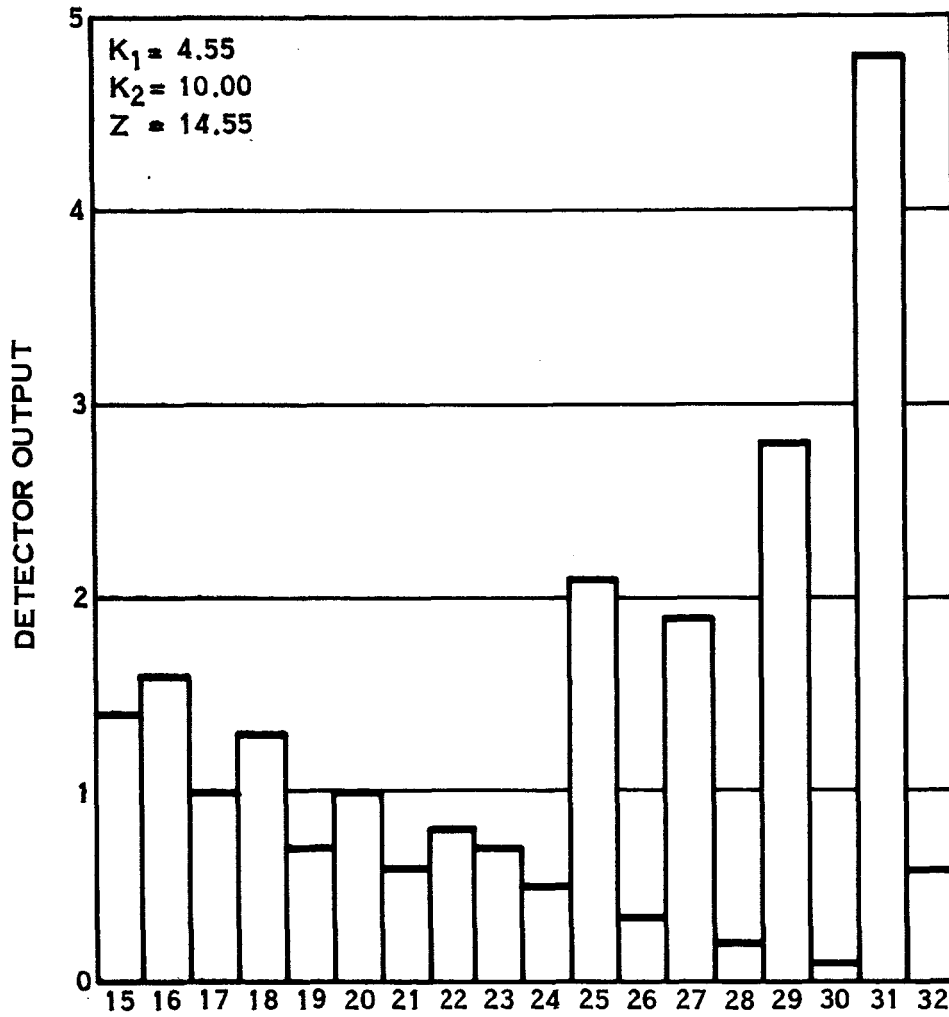


FIGURE 4. DIGITIZED CHROMATOGRAM BAT GUANO

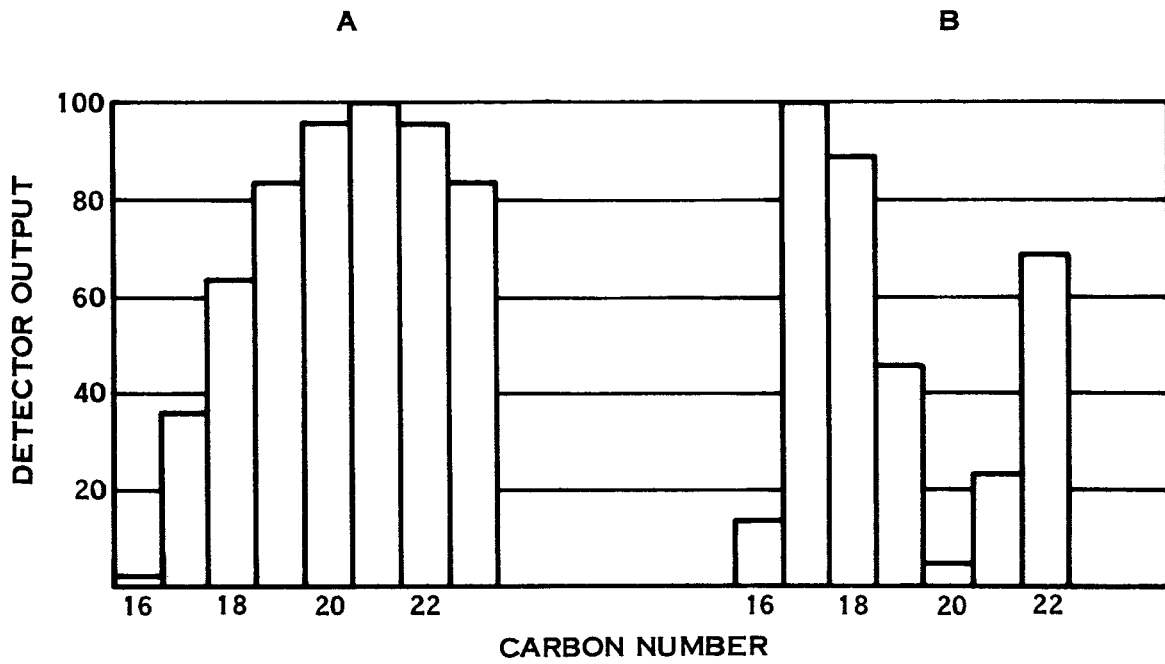


FIGURE 5. TWO DUMMY CHROMATOGRAMS

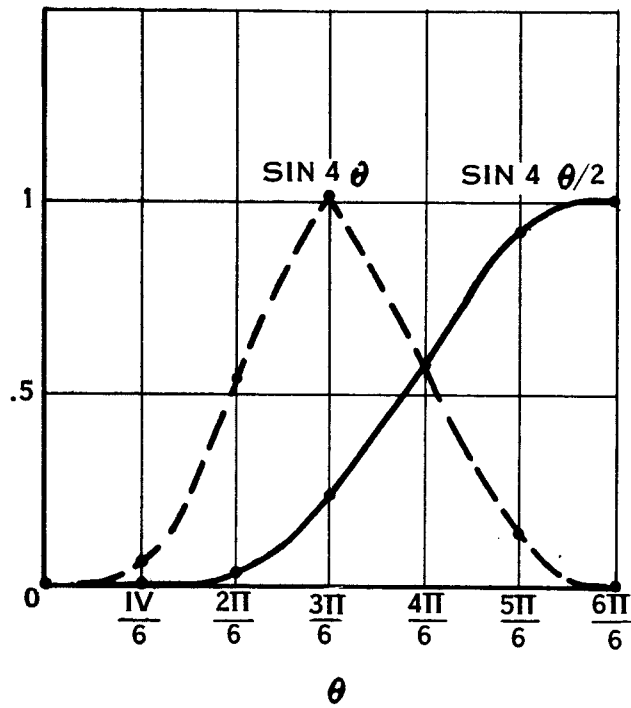


FIGURE 6. DIGITAL FILTER POWER TRANSFER FUNCTIONS

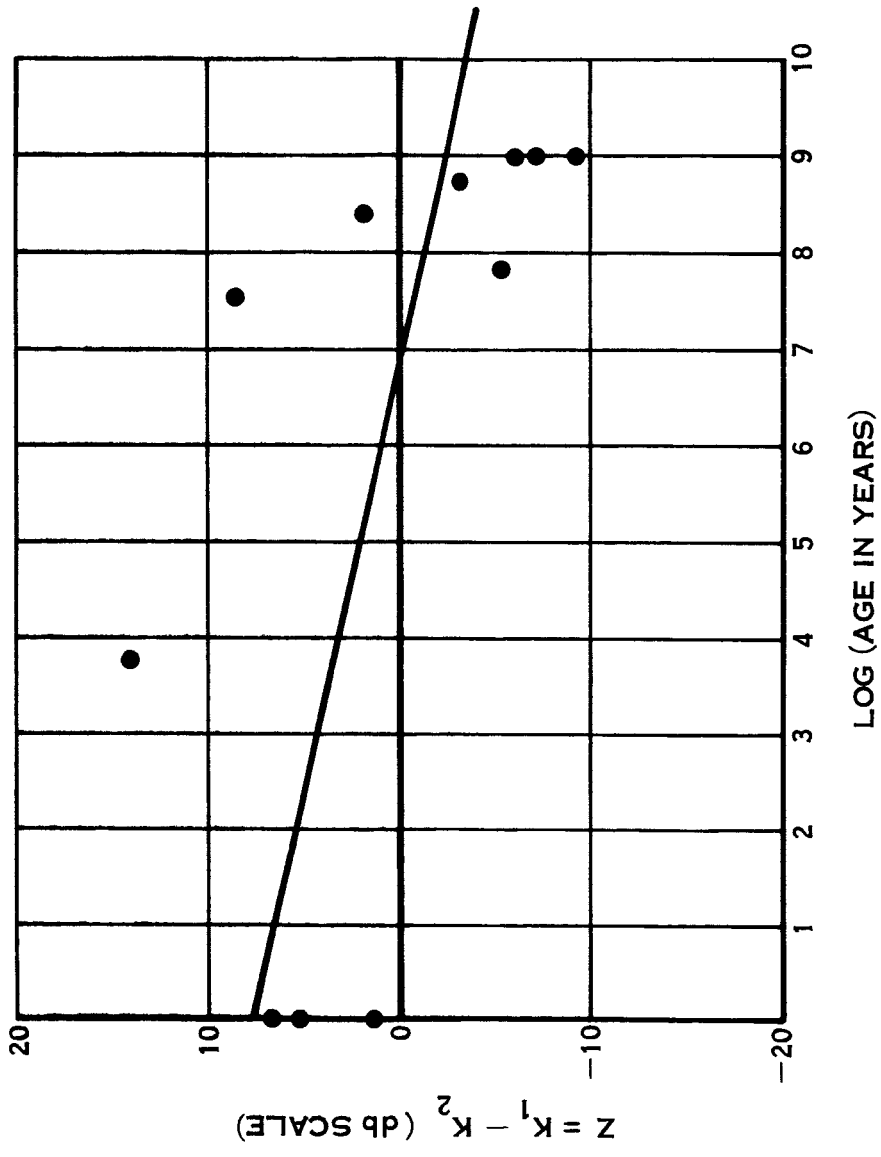


FIGURE 7. BEHAVIOR OF $Z = K_1 - K_2$ WITH AGE

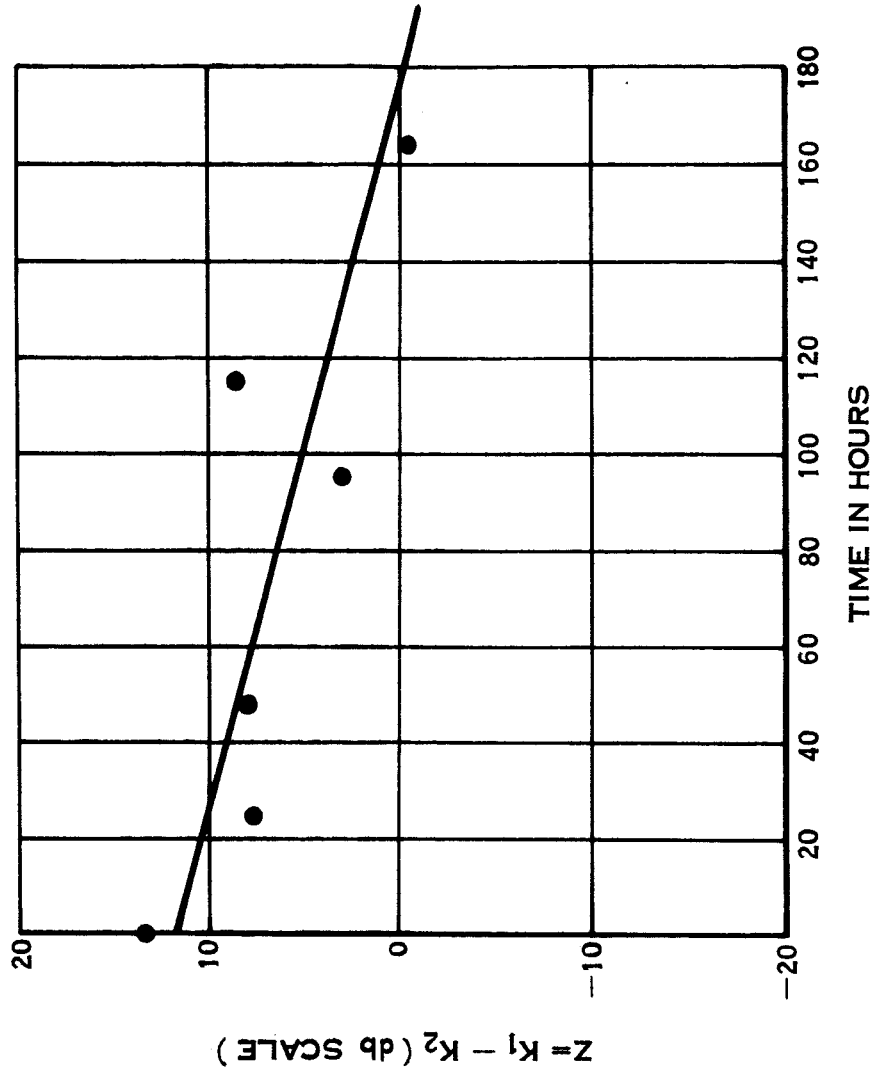


FIGURE 8. BEHAVIOR OF $Z = K_1 - K_2$ UNDER EXPOSURE TO 350°C FOR VARIOUS TIMES

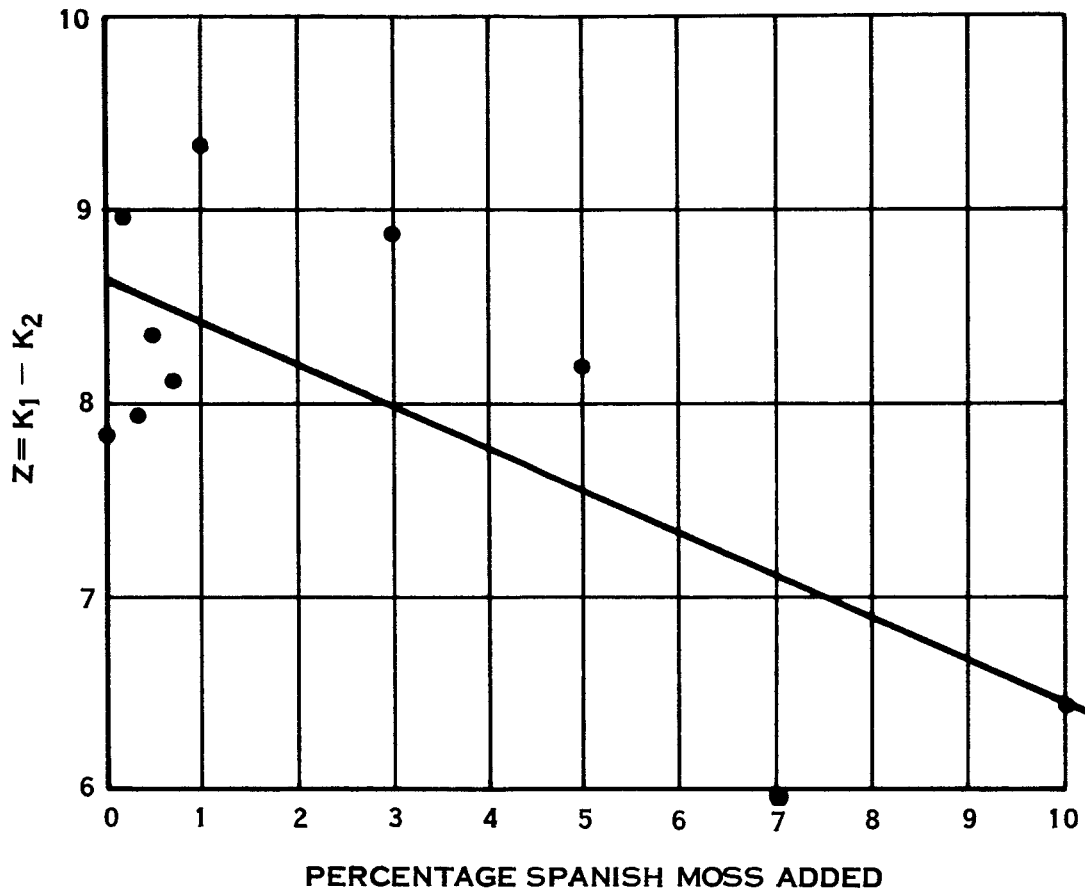


FIGURE 9. REFINERY WAX PLUS SPANISH MOSS

3.0 SURVEY OF INSTRUMENTS FOR IMPLEMENTING A MARTIAN ATMOSPHERIC
COMPOSITIONAL ANALYSIS EXPERIMENT FOR LIFE DETECTION

3.1 Introduction

Because previous studies* indicate that analysis of the Martian atmosphere, provided it is complete and sensitive, might provide direct evidence of Martian life, some of this reporting period's efforts were devoted to verifying the practicality of such an approach to life detection by discovering whether suitable techniques are available for implementing this experiment. These activities were conducted in conjunction with Dr J. E. Lovelock# and Dr. Peter B. Fellgett**, both of whom acted as paid consultants to the project. Dr. Lewis D. Kaplan## and Dr. Janine Connes*** and Dr. Pierre Connes### acted as unpaid consultants and devoted considerable time and effort to this portion of the studies.

This study initially consisted only of reviewing the possible role of the envisaged experiment in the Martian exploration program, and of surveying a small number of experiments already under development for inclusion in Voyager payloads. It very soon became obvious that while none of these instruments are satisfactory, an entirely new technique, namely Fourier Transform Spectrometry using ground based IR observations of the planets, appeared to offer enormous potential advantages over instruments carried by Martian landers or orbiters and to be capable of providing all the data needed. Although the very great advantages of this technique over conventional slit spectrometry are well established, relatively little consideration of its possible role as an adjunct to the current planetary exploration program appeared to have been made. Consequently, the scope of this instrument survey was expanded to include a more detailed consideration of the possible ways in which Fourier Transform IR spectrometry could contribute to the Voyager program, including a brief exploration of parameters relevant to the design and construction of satisfactory IR observation systems.

* Reported in detail in another section of this document.

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** Professor of Applied Physical Sciences, University of Reading, Reading, England.

Jet Propulsion Laboratories.

***Observatoire de Meudon and Centre National de La Recherche

###Scientifique, Bellevue, S & O, France.

3.1 (continued)

This expanded study is not yet complete. Its findings will be the subject of a special project report authored by the five consultants listed above together with project personnel. Partial preliminary results of this study are presented below. They consist of a specification of the information the proposed experiment should provide (including a summary of the reasons why it is viewed as a life detection experiment), a discussion of the utility of this information to the Martian exploration program, a summary of the cost and scheduling restrictions which such an experiment should satisfy in order to be of optimal value to the program, and an evaluation of four instruments considered and rejected as candidates for implementing the proposed experiment.

3.2 Objectives Of The Martian Atmospheric Analysis Experiment And Their Relationship to The Voyager Program

The first step in this survey program consisted of specifying the objectives of the proposed experiment and the conditions it must satisfy in order to be judged feasible, in such a way as to make it possible to compare the relative advantages and disadvantages of alternative implementations.

Initially the proposed experiment was considered only in the context of the search for Martian life, and the objectives were considered only from the point of view of the possibility of making valid biological interpretations of the data supplied. Shortly after its initiation it became apparent that the study might result in recommending an entirely new program of ground-based IR observations of the planets, which conclusion might be viewed by many as representing an unorthodox departure from the current focus of the NASA planetary exploration program, namely inquiries implemented by space probes. Anticipating that such a significant departure would require considerable justification, we extended our scope of inquiry to include the general utility of the experimental results not only to the life detection mission, but also to other objectives of the exploration program, and, most important, to the need to "explore the planet in an efficient way, putting priority of the surveys and experiments that have maximal relevance to later scientific investigations."*

*Space Research: Directions for the Future Report of a study by the Space Science Board, Woods Hole, Mass., 1965 NAS-NRC Council, December, 1965, p. 12.

3.2 (continued)

The conclusions of this portion of the study are:

1. An atmospheric analysis experiment which identifies all the major and trace components present down to concentrations of 10^{-8} or 10^{-9} (with the possible permissible exception of the chemically inert rare gases) and provides an estimate of their concentrations accurate to $\pm 0.1\%$ for major components and ± 3 db. for trace components present in concentrations of 10^{-5} or less may detect life on Mars if it is present. This should be the first exobiological experiment conducted because it is the most general one available, in that it places fewest restrictions on the nature or location of the biota it is capable of detecting, and because its results will greatly influence the selection of subsequent exobiology experiments.
2. Such an experiment, whether or not it detects life, will provide results of major importance to the planning of a logical and systematic program of planetological inquiry because the composition of the atmosphere influences and reflects physical and chemical processes occurring in the atmosphere and at the atmosphere surface boundary, so that detailed knowledge of the atmospheric composition can be expected to lead to improved insight into the chemistry, meteorology, physics, and geology of the planet and to help establish priorities among the available strategies of inquiry.
3. Given that atmospheric compositional information is of great potential relevance to both the biological and non-biological objectives of the Voyager program, the value of such information is in part a function of whether or not it can be made available early enough in the planning cycle to be used in the design and selection of follow-up experiments, therefore, any experiment capable of early implementation has significant advantages, and in particular, any which do not need to be carried on board a spacecraft would clearly be of great value.

The considerations which lead to these conclusions are presented in the following sections.

3.2.1 Life Detection By Atmospheric Compositional Analysis

Recent studies* of the potential biological significance of measurements of purely physical parameters have revealed that the atmosphere of the Earth provides direct and highly conclusive evidence of the presence of life. This conclusion follows from the observation that while 20 per cent v. of the atmosphere is oxygen, it also contains quantities of reduced gases of which one, namely methane, (which is present to the extent of 1.5 parts per million) cannot exist in reversible equilibrium in an oxidizing atmosphere. The formation of methane from the hydrogen

*Reported in more detail in section 2 of this document.

3.2.1 (continued)

and carbon compounds in the atmosphere requires a sequence of at least four reactions, and the intermediate compounds in this sequence must all be partially oxidized organic compounds or free radicals whose probability of surviving long enough to encounter the rare molecule necessary for the next step before being oxidized by the abundant oxygen or decomposed by UV radiation is extremely unlikely.

Although methane is stable in the lower atmosphere, it is oxidized by monatomic oxygen at levels where that constituent is prominent and is dissociated by UV radiation in the upper atmosphere. Consequently the observed concentration implies the existence of a significant methane production mechanism in the lower atmosphere. For example, a methane oxidation rate which leads to a total turnover of atmospheric methane only once per thousand years corresponds to 10^9 molecules $\text{cm}^{-1} \text{sec}^{-1}$. But from the fact that methane is irreversibly oxidized in the atmosphere it follows that this mechanism is not an atmospheric one, nor does it take place at any point on the surface in contact with the atmosphere. Reaction of iron carbides with water could produce some methane, but in order to account for the observed concentration the supply of iron carbides would have to be very large and constantly replenished. Solid phase reactions occurring beneath the surface are similarly too slow.

The methane could not have been produced during the period when the earth had a reducing atmosphere and somehow preserved beneath the surface now to appear as an outgassed product, because it would not survive the temperature and pressure conditions to which it would be subjected, and it is difficult to conceive of a process which could account for its storage; furthermore, outgassing at the estimated conservative rate of oxidation for as little as 5×10^8 years would require the storage of an amount of methane equal to four times the total mass of the current atmosphere. Thus the simultaneous presence of methane and oxygen cannot be readily accounted for as the result of abiological processes expected to occur on a planet devoid of life.

If, however, we assume that a fundamental and general characteristic of life is its ability to establish and maintain a free energy gradient and to power biological functions by means of the controlled use of the energy potential thus established, then the presence of the energy gradient represented by the simultaneous presence of methane and oxygen may be interpreted direct evidence of the presence of terrestrial life. This conclusion is consistent with the observation that although the production of methane must be a gas or liquid phase reaction (solid phase reactions being too slow to account for its concentration) its production takes place below that region where solar energy capable of effecting rapid reactions among gaseous constituents is available. This implies that if the solar flux is the ultimate source of the energy used to produce the free

3.2.1 (continued)

energy gradient between atmospheric methane and atmospheric oxygen, this energy must be utilized in a highly organized and, physically speaking, unlikely fashion. Although such a process is, as has been pointed out, so unlikely as to be virtually impossible on a planet devoid of life, the conclusion that it is in fact effected by a biota is wholly consistent with the view that life forms are highly organized, one of whose implications is that they are able to effect energy transformations which only rarely if ever occur in non-living systems.

The observed methane-oxygen system provides an additional argument for the existence of a terrestrial biota as a mechanism which replenishes the oxygen consumed in methane oxidation. Although aeronomists have for many years searched for an abiological mechanism to explain the transition from a reducing to an oxidizing atmosphere, the only one which can explain net increase in oxidation is the escape of hydrogen which can be derived from photolysis of H_2O in the upper atmosphere. The argument for the biota as a source of oxygen to oxidize methane derives from the fact that the current estimates of hydrogen escape--- 2.5×10^7 atoms $cm^{-1} sec^{-1}$ ---are far too low to provide the oxygen needed to effect a total turnover of atmospheric methane in a period of time as long as 1000 years. If only three atoms of oxygen are required to oxidize each molecule of methane, the resulting consumption is (at least) 3×10^9 molecules $cm^{-1} sec^{-1}$, which requires a hydrogen escape rate more than two orders of magnitude greater than that estimated. It will be observed that this argument is less strong than the one presented above in that it assumes knowledge of the structure of the atmosphere on which to base an estimate of hydrogen escape and depends on accurate knowledge of the concentration of methane. If the concentration of methane were lower, or if it were not known with great accuracy, this conclusion could not be drawn.

Certain other constituents of the terrestrial atmosphere-- CO , H_2 and N_2O --are somewhat suggestive of terrestrial life, but do not provide by themselves strong evidence because, unlike methane, all of them can be expected to occur at some concentrations in an atmosphere containing in addition CO_2 , H_2O and N_2 and O_2 . Not enough is known about the atmosphere to determine whether the observed concentrations are inconsistent with the hypothesis that their presence is due entirely to abiological causes. All that can be said at this point is that CO and H_2 are gasses which would be characteristic of reducing atmospheres, and therefore their presence in atmospheres containing large amounts of oxygen seems somewhat anomolous. The possible biological significance of N_2O is that its lifetime in the atmosphere is short because it is destroyed by comparatively long wavelength UV radiation; the calculated removal rate being 10^{11} molecules $cm^{-1} sec^{-1}$. Although a number of atmospheric reactions have been proposed to account for the occurrence of all these constituents, the question of their origin does not appear to have been finally settled. It

3.2.1 (continued)

should be noted here that if the abundance profiles of these constituents were known, where in the atmosphere they originate and where they are removed could perhaps be determined. In particular, the rate of change of concentration might by a sufficiently sharp function of altitude determine whether their concentrations are affected by any production or removal processes occurring at the surface. The biotic significance of surface reactions on earth is that this region is shielded by the atmosphere from solar radiation capable of effecting chemical reactions among the atmospheric constituents, and consequently any chemical reactions of a magnitude sufficient to give rise to detectable gradients can be attributed to the action of the biota. (This would not necessarily be true of Mars.)

3.2.2 Possible Biological Significance Of Martian Atmospheric Experiment

Whether or not a Martian biota, assuming one exists, can be detected by an analysis of the composition of the Martian atmosphere depends necessarily upon the nature of the Martian biota and on the degree of its interaction with the atmosphere as well as upon the completeness, accuracy and reliability of the experimental results.

Although it cannot be proved that the proposed experiment will necessarily detect any Martian life form which may be present, the conditions which must be satisfied in order for its presence to be reflected in the atmosphere seem minimally restrictive. The most fundamental assumption is that all life is characterized by the ability to establish and maintain a free energy gradient, and that living organisms release this energy in controlled reactions which power biotic processes. In addition, the postulated Martian biota must satisfy the following conditions:

1. It is chemical in nature, composed of chemical substances made up of elements readily available in the environment in the form of stable molecules, and the potential energy utilized to power biotic processes is stored in the form of chemical free energy.
2. The solar flux is the ultimate source of the energy used by the biota. This solar energy is biotically transformed to chemical energy by means of a process which uses available radiation to dissociate strongly bound stable molecules into reactive dissociation products that are then stored. This solar to chemical energy conversion process takes place at or near the surface.
3. At least some of the stable molecules dissociated in this energy conversion process are derived from the atmosphere.
4. At least some by-products of energy releasing biochemical reactions are released into the atmosphere.

3.2.2 (continued)

5. The fundamental energy conversion process also releases some of the reactive dissociation products into the atmosphere, so that the resulting chemical free energy gradient is one between the organisms and the atmosphere.

That a Martian biota, if one exists, will satisfy the first two conditions seems obvious. The third--that stable atmospheric molecules are used as raw materials--seems reasonable in view of the fact that gas and liquid phase reactions, being faster than solid phase reactions, would more efficiently utilize available solar energy, which suggests that gases are likely to be used as raw materials. Atmospheric constituents are readily available at the surface where the energy conversion probably takes place, and the supply of atmospheric raw materials is regularly replenished. Furthermore, it can be argued that the preferred elements would be those common elements capable of complex molecule formation, namely C, N, H, O, S, and P; most of the stable molecules of these elements are gases.

The fourth condition--that some by-products of energy releasing biochemical reactions are released into the atmosphere--also seems reasonable given the assumption that most biochemical reactions are gas or liquid phase reactions. Unless all by-products of all biotic chemical reactions are conserved (which seems unlikely since many of these must be waste products which are either energy-poor or not capable of efficient further biotic processing) some must be excreted, either as liquids which subsequently volatilize or directly as gases.

That a Martian biota would satisfy the last condition by releasing reactive dissociation products directly into the atmosphere during the basic solar energy to chemical energy conversion also seems reasonable but is by no means certain. It is conceivable that Martian life forms have evolved a way of storing all the reactive dissociation products. This would be analogous to storage by terrestrial green plants of all the oxygen they produce in photosynthesis as well as all of the reduced carbohydrates. This would limit the site of energy release to the point at which energy conversion occurred, and would require that all the dissociation products produced biologically are also consumed by the same organism or one contiguous to it. Although many objections can be urged against such a scheme, it is not totally inconceivable. It will be observed that the release of some of the reactive dissociation products into the atmosphere has the advantage that they will tend to be readily available when and where they are needed and will be locally replenished as they are consumed in the controlled recombination reactions.

If all these conditions are satisfied then the Martian atmosphere will contain biological "contaminants" derived both from the solar energy

3.2.2 (continued)

conversion process which established the initial chemical energy gradient, and from subsequent energy releasing reactions. The resulting atmospheric mixture will contain at least some incompatibles analogous to the presence in the terrestrial oxidizing atmosphere of reduced gases. Whether any of these will be as recognizably unlikely a constituent of the Martian atmosphere as methane is of the terrestrial atmosphere cannot be determined in advance since some of the contaminants may be so unfamiliar that recognizing their biotic origin may require additional study or additional knowledge of Martian conditions. It should also be noted that in addition to contaminating it with unusual products, the Martian biota may also remove from the atmosphere constituents which under abiological conditions would be expected to accompany those observed.

At this point it is not possible to anticipate the specific kinds of additional information which may be required for a complete determination of the biological significance of the atmospheric composition. The chemical composition of surface matter and the effects of the solar flux on the surface-atmosphere chemical reactions will be of interest, although the fact that the surface can be expected to be in a state of near chemical equilibrium with the atmosphere if there is no life on Mars should narrow the range of possibilities.

It is clear that in order to provide adequate data for the kind of biological interpretation outlined above an atmospheric compositional analysis experiment should permit identification of all the major and trace constituents present down to concentrations on the order of 10^{-8} or 10^{-9} , with the permissible exception of the chemically inert rare gases. Accuracy of concentration measurements need not be great; $\pm 0.1\%$ will suffice for major constituents and ± 3 db. for trace constituents present in concentrations of 10^{-5} or less.

It will be obvious that if this kind of atmospheric life detection experiment can be implemented, it will have a great many advantages compared to more conventional life detection experiments under development. Among these are:

1. It is very general in the sense that it places very minimal restrictions on the kind of life it is designed to detect. In particular, it does not make any assumptions regarding the basic biochemistry of that life, its physical distribution, density, or its response to environmental conditions.
2. This experiment is not site limited. The atmosphere will reflect processes occurring on the whole surface of the planet and it is not necessary to sample the atmosphere in a locale characterized by a high density of biological activity.

3.2.2 (continued)

3. This experiment will provide information of relevance to all subsequent biological experiments; even if it does not provide unambiguous evidence of a biota, it will aid in specifying those conditions under which specific life processes can be best demonstrated. For example, an experiment designed to demonstrate growth or oxidative metabolism in an aqueous medium is hardly likely to prosper if the local conditions are anhydrous, highly reducing and at a mean temperature of -40°C . Alternatively, positive identification of atmospheric biological contaminants will reveal the major features of the fundamental chemical energy gradient utilized by the biota, from which some of the more probable metabolic pathways might be inferred.

The great generality of this experiment as a life detection experiment, and the utility its results to the design of subsequent experiments in the biological exploration of the planet strongly imply that it should be the first in the sequence of biological experiments conducted. The advantage of conducting it as soon as possible so that its results can be employed most efficiently need not be stressed.

3.2.3 Other Uses Of Atmospheric Compositional Data

The discussions above have concentrated on the use of Martian atmospheric compositional information in drawing conclusions about the biology of Mars. This role has been emphasized because it places very stringent conditions on the catholicity and sensitivity of the experiment, and because the orientation of this project is a biological one. However, an experiment which satisfies the requirements of the biological mission can be expected to have great significance for the non-biological objectives as well. Thus, the process of understanding the biological significance of the atmosphere is one of explaining the presence of any chemically active constituents in terms of surface and atmospheric reactions which account for their presence and, roughly, their concentrations. Any hypotheses offered will have non-biological as well as biological implications. In particular, there will be important implications regarding the nature of the chemical and physical composition of the surface, particularly as regards the effects of condensible gases which may precipitate out on the surface. When combined with temperature and heat flow measurements, such data may go far toward understanding the seasonal color changes and delineating the effects of the observed changes in the polar caps, and, in general aid in identifying and classifying the major physiographic features of the planet. The probable intensity of solar radiation reaching the surface, and its effects on precipitated condensible gases can in part be estimated from detailed knowledge of the composition and density of the atmosphere. Similarly, improved understanding of the meteorology of the planet can be expected to follow the availability of detailed compositional data, and useful predictions regarding the dynamic structure of the atmosphere, including wind velocity and erosion of surface features, could be

3.2.3 (continued)

partially based on such information.

As in the case of the biological implications of the atmospheric composition, it is not possible to anticipate all the non-biological implications of the results of the proposed experiment. They necessarily depend on what those results are. But that the results will be useful, and will lease to a host of specific testable hypotheses regarding subjects of major interest in the scientific exploration of the planet is a virtual certainty. In fact, it is difficult to think of any other single experiment whose findings would be of greater or more widespread significance to the entire exploration program.

3.3 Cost And Planning Restrictions

In order to be practical, the envisaged atmospheric compositional analysis experiment must satisfy the budgeting and planning schedules of the current Voyager program. Rules of thumb regarding what are viewed as permissible cost levels and target schedules were generated after a brief survey of tentative Voyager plans in effect in late 1965, which were very generously provided by C. Campen of the JPL Voyager Project Office.

3.3.1 Cost

Two bases for estimating permissible costs were employed.

The proposed experiment may be compared with other experiments being developed for inclusion in Voyager payloads. Experience indicates that the cost of the science sub-system (independent of the cost of capsule, spacecraft, or booster), is a linear function of its weight. Thus, the money required to design, engineer, produce and test the necessary sequence of laboratory and flight versions of the instruments selected is estimated to cost between \$250 and \$500 thousand per pound, the higher estimate being viewed as the more likely one if the instruments are to be soft landed. The reference weight selected for this comparison is that of a double focus mass spectrometer, since this is the most sensitive and catholic of the instruments available for atmospheric compositional analysis. Because this instrument must be deployed on the surface after soft landing (because it does not operate rapidly enough for reliable sampling and analysis during descent) the resulting comparison figure is \$3.75 million. This, then, may be taken as a reasonable figure for an experiment which does not provide results earlier than the time of deployment of the first planned Voyager lander.

If the experiment does not require inclusion in a Voyager payload, a somewhat higher figure may be considered reasonable, particularly if it provides early results. One method of arriving at such a figure is to consider the cost of a 7.5 lb. mass spec as a prorated

3.3.1 (continued)

function of the cost of an entire Voyager system, including Saturn V booster, spacecraft and capsule. Such a system capable of landing a 250 lb. payload on the surface of Mars is estimated to cost between \$570 and \$640 million, or 2.25 to 2.56×10^6 dollars per pound if the first shot is successful, or 4.3×10^6 dollars if two shots are required. Using the lower figure and the reference weight of 7.5 lbs., we arrive at a total of \$17.25 million, which may reasonably be said for comparison purposes to represent the cost of performing atmospheric compositional analysis by mass spec on the surface of Mars.

An alternative way of arriving at a reasonable cost figure for an experiment which does not require transportation to the surface of Mars is in terms of its cost relative to the total Voyager program. Thus, if it is believed that ground based IR observations can be provided early enough to be of planning value, a policy of investing a total equivalent to one or two percent of the Voyager program costs might be justified. This is 10 to 20 million dollars if the current Headquarters estimates of \$1 billion are accepted.

3.3.2 Target Schedule

The restrictions which determine how far in advance information should be available if it is to be used effectively are a function of the time prior to launch at which significant design decisions are frozen. The most important decisions and their timing relative to the launch date are:

Start Design of Spacecraft	4.5	years	in	advance
Finalize Payload Selection	4	"	"	"
Freeze Interface Specs	3.5	"	"	"
Deliver Final Flight Configuration	2	"	"	"
Enter Final Testing	1	"	"	"

Clearly, the two most important events from the point of view of payload selection and design are the payload selection itself and the freezing of interface specifications. (Interface specifications cover weight, size, shape, thermal requirements, power requirements, data rates and control functions). Certain very minor changes in the experiments may be made up until the time that the final flight configuration is delivered.

A certain amount of lead time must be allocated to interpreting the results of the compositional analysis experiment, determining their significance for the selection of the final payload, and translating these into payload options. The lead time required clearly depends upon the nature of the results, but two years would seem to be a reasonably generous estimate. From this it follows that the optimum time to have these results is six years in advance of scheduled launch, but that information may still be of great value up to about 4.5 years in advance, assuming that a minimum of time is required

3.3.2 (continued)

to interpret the results and they do not imply the need for the development of a completely new payload concept. Results available as late as four years in advance may still be used to advantage in modifying experiments selected for payload inclusion; it should be observed that even if the results of the experiment envisaged are provided too late to have any direct effect on the planning of a Voyager mission, they still will be of inestimable value in interpreting the data acquired by the landed instruments.

If we assume that 1973 is the anticipated launch date for the first Voyager mission, then 1967 is the optimum time for obtaining Martian atmospheric compositional data, a date which clearly cannot be met. The earliest practical target has, therefore, been selected as late 1968 or early 1969. The possibility of meeting this targeted date is the subject of a discussion in the forthcoming special project report mentioned above.

3.4 Techniques Under Development: Mass Spectrometry And Gas Chromatography

Atmospheric analysis instruments currently under development were briefly reviewed and eliminated as candidates for the proposed experiment. Four classes of instruments developed for inclusion in probes were considered. Two of these--an oxygen detector and a water vapor detector designed for atmospheric sounding--were immediately eliminated because they detect only one component of the atmospheric mixture. Two other more catholic detectors were also considered and rejected, for the reasons discussed below.

3.4.1 Gas Chromatograph

GC's are being designed for a variety of modes of use; that for atmospheric analysis will probably use a thermal conductivity detector with a maximum sensitivity (for constituents with the highest molecular weight) of 1×10^{-7} , which is believed, for this application, to be marginal. The most severe disadvantage of the GC is that it can effect reliable identification of only a preselected set of constituents. Currently GC's are designed to detect only the atmospheric constituents N_2 , O_2 , Ar, CO_2 , H_2O , CH_4 , NH_3 , N_2O , NO, NO_2 , HCN, CO, H_2S , and SO_2 , which are the constituents named by the Space Sciences Bioscience Subcommittee. If additional constituents are present, they will not be detected unless current designs are specifically modified to permit their identification, which requires a lead time of about two years. This limitation is felt to be crucial, since the biological interpretations outlined above can be made successfully only if all constituents are identified, and if a biota is present the biological contaminants are very likely to be quite surprising ones. Furthermore, the restricted nature of the GC's response will make it difficult to interpret the data which is provided reliably, since it cannot be assumed that those constituents detected are all the constituents present.

3.4.2 Mass Spectrometer

The mass spectrometer currently under development at JPL is a far more catholic instrument than the GC, in that it is able to respond to almost all the gaseous constituents which could be present in the atmosphere. (Like the GC, it is blind to He and H₂.) The primary limitation of the responsiveness of the mass spec is the problem of interference; e.g., CO is very difficult to detect in the presence of N₂ or CO₂, and CO₂ tends to interfere with oxides of nitrogen. Since identification depends upon the fragmentation pattern and two otherwise similar components may differ in the presence or absence of very small peaks at some mass numbers, the sensitivity of this instrument to some components of a mixture is in part a function of the identities and concentrations of the remaining components. The single focus instrument currently being built could almost certainly detect and identify anything down to a concentration of 10⁻³ (except for the interference problem mentioned above). A double focus instrument which is heavier (7.5 lbs. vs. 5 or 6 lbs.) and more complex could probably insure detection of constituents down to 10⁻⁶. This instrument was, therefore, rejected on the grounds of inadequate sensitivity and because the interference problem was considered critical.

APPENDIXD R A F T

ANALYSIS OF THE MARTIAN ATMOSPHERE: ITS BIOLOGICAL SIGNIFICANCE

D. R. Hitchcock* and J. E. Lovelock**

There is wide agreement among space scientists whose primary orientation is towards the physical sciences, that experiments to observe the physical properties of the surface and atmosphere of Mars should be given high priority in the Martian exploration program. It is not so widely recognized, however, that these experiments could, in principle, yield useful information to biologists whose primary concern is to determine whether life exists on Mars, and, if so, in what form.

To understand the kind of life that may exist on Mars, information must be obtained about those properties of its surface and atmosphere to which any evolving Martian must have become adapted. It is not always realized that such information, by providing evidence of effects that cannot be accounted for by abiological processes, could constitute direct and primary evidence of life.

Observations of purely physical properties may provide information supporting the hypothesis that life exists on Mars: this follows directly from a fundamental and highly plausible assumption, that the entropy of living systems is low relative to that of their non-living environments (1). This assumption has two relevant consequences: firstly, that living systems will drive their environments into physical or chemical disequilibrium, recognizable as such if existing data are sufficient to rule out explanations of their state in terms of abiological processes; and, secondly, that there will always exist an entropy gradient between living systems and their non-living environments. The origin of non-living biogenic material will be revealed by the existence of such a gradient for a time which will vary according to the rate of attainment of equilibrium, as determined by local conditions, but which can be expected to be measurable in units of at least 10^3 years and thus, probably, be long compared to the lifetimes of the organisms themselves.

Given that the presence of life is characterized by a state of physical and chemical disequilibrium of the system, life plus environment, can essential disequilibria be effectively diagnosed from practical observations? If life exists on Mars, the atmosphere of Mars is likely to be an important part of the environment and its composition should reflect the presence of life forms, on the plausible assumption that they continuously react either directly or indirectly with it. The object of this paper is critically to review the potential biological significance of two types of atmospheric data: those which concern the relationship between the atmosphere and the surface material, as revealed by experiments designed to detect a free energy gradient between

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the two; and those which concern the concentrations of major and trace components of the atmosphere. Although the two types of experiments from which such information should be obtainable differ greatly in terms of their implementation, interpretability and potential biological significance, they both represent ways of implementing a strategy of life detection based on a search for evidence of disequilibria. Both also depend on the assumption that the atmosphere is a relatively homogeneous medium which reflects processes occurring over the whole surface of the planet.

LIFE DETECTION BY MEANS OF DETECTION OF CHEMICAL FREE ENERGY IN SURFACE MATTER

One of the consequences of the assumption that the entropy of living systems is low relative to that of their non-living environments is that there will always exist an entropy gradient between the two. After death, the free energy stored in a living system is gradually dissipated into the surrounding environment until, eventually, the matter which once comprised the living system ceases to have a relatively low entropy.

The most likely site for life on a planet is the interface between its surface and the atmosphere where the solid, liquid and gaseous phases meet at the point of maximum absorption of solar energy, maximum temperature and where a diversity of raw material, provided by both the relatively mobile atmosphere and the less readily transported surface matter, is available at the same time as the energy necessary for their biotic transformation.

The synthesis of biotic compounds from simple abiotic molecules requires the dissociation of the latter and the build-up of some of the reactive dissociation products into large complex molecules. The dissociation of simple inorganic molecules, such as water and carbon dioxide, not only releases reactive products to be used in the synthesis of biological molecules, but also simple active molecules like oxygen into the atmosphere. These two processes result in the storage of chemical free energy in the biotic molecules, which are large and relatively non-volatile and hence tend to accumulate at the surface-atmosphere interface. Life, therefore, tends to generate a sharp metastable chemical free energy gradient between the surface and the atmosphere.

Perhaps the simplest experiment in life detection, therefore, is to look for a chemical free energy difference between Martian surface matter and atmosphere. A promising experiment consists of equally heating two aliquots of surface material, one in an inert gas such as argon or nitrogen, the other in the Martian atmosphere, and recording the temperature of each sample. A combustion reaction between the sample and its own atmosphere would produce an excess of heat, whereas heat changes due to chemical transitions in the surface matter would be equal in both samples. The occurrence of such a combustion would be detected by a difference in temperature between the sample heated in the atmosphere and that heated in the inert gas. If the planet were to have a reducing atmosphere, a lesser but still observable evolution of heat could be expected from the reduction of the more oxidizable, metastable biotic molecules. If the constituents of the atmosphere were known, additional information could be obtained by noting the temperature at which

the combustion occurred and by examining the volatile pyrolysis products.

It is debatable whether such an experiment is subject to false positives of any sort except, of course, those resulting from machine errors or inadvertent contamination of the equipment before launching. For example, sulphide rocks will burn on heating in air although their ignition temperature is different from that of organic matter. On Earth, however, at least some sulphide rocks are thought to be of biological origin. It would seem that if the fundamental assumption on which this experiment is based (that life can be defined in terms of its entropy-reducing function) is valid, evidence of chemical free energy gradients between surface matter and atmosphere should always be construed as prima facie evidence of life.

ANALYSIS OF THE MARTIAN ATMOSPHERE

Experiments designed to identify and determine quantitatively the major and trace components of the Martian atmosphere may be recommended on many grounds. The utility of such measurements to scientific programs not primarily concerned with Martian biology need not be stressed. They are, however, essential for the satisfactory interpretation of analyses of surface material, bacteriological experiments and other experiments designed to demonstrate the existence of Martian life forms by their direct observation.

The assumption that the atmosphere of Mars, like that of Earth, is relatively homogeneous implies that such atmospheric experiments are not likely to be site-limited. The probability of such an experiment being performed near an active volcano and, hence, of results being recorded that could not be extrapolated to other locations, is negligible. Moreover, such a situation would be recognized from other available information and the results of the experiment could still be usefully interpreted. For these reasons attempts to analyze the Martian atmosphere deserve high priority. The primary disadvantage that may be urged against such experiments as part of a biological program is that they are unlikely to provide direct or relatively conclusive evidence of life on Mars.

As already mentioned, one might, on very plausible theoretical grounds, suppose that life forms in continuous interaction with the atmosphere would drive it into chemical or physical disequilibrium, recognizable as such if observations of its state were sufficiently complete. The claim that an analysis of the atmosphere of Mars can provide information which can be interpreted as indicative of the presence of life forms deserves critical examination. Analysis of the Martian atmosphere cannot be advocated as a good means of detecting life if terrestrial atmospheric information does not provide good evidence for the existence of terrestrial life. If, however, a good case can be made that terrestrial life can be demonstrated from the analysis of the terrestrial atmosphere, analysis of the Martian atmosphere ought to receive very high priority as an exobiological experiment and care should be exercised to ensure that the experiments are designed to provide the greatest amount of potentially significant biological information.

The arguments presented above suggest that atmospheric evidence of life will take the form of an observable free energy gradient which is anomalous

in that it cannot be accounted for in terms of the abiological processes which could be expected to occur on a planet devoid of life. For example, the simultaneous presence of two gases which, like hydrogen and oxygen, are chemically incompatible, is evidence of such a gradient. Whether it is an anomalous gradient is, however, somewhat less easy to determine. Such a determination requires a model of the abiological steady state atmosphere which takes into account those departures from simple thermodynamic equilibrium which can be attributed to the action of the solar flux and related atmospheric transport phenomena. Any constituents whose concentrations are not accounted for by such a model could then be construed as evidence of life. Unfortunately, the current status of aeronomy is such that we must seriously question any proposed model of an abiological steady state atmosphere. At this moment, therefore, one cannot clearly identify all those atmospheric constituents whose concentrations can be accounted for only on the hypothesis that life exists on Earth. But the question is not whether one can identify all the atmospheric constituents whose observed concentrations are incompatible with the hypothesis that there is no life on Earth. The question is rather, can at least one constituent be identified, for it is clear that if one cannot be explained on abiological grounds, the whole atmosphere of which it is a part can be said to depart from abiological equilibrium and, therefore, provide evidence of life.

TABLE I

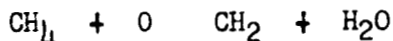
Chemically Active Components of the Earth's Atmosphere

<u>Gas</u>	<u>Ratio by Volume</u>	<u>Remarks</u>
N ₂	0.78	Mixed in troposphere
O ₂	0.21	Mixed in troposphere
CO ₂	3 x 10 ⁻⁴	Mixed in troposphere
H ₂ O	10 ⁻⁵ to 10 ⁻²	Dissociates in mesosphere
O ₃	10 ⁻⁷ to 10 ⁻⁸	Peak in stratosphere
CH ₄	1.5 x 10 ⁻⁶	Dissociates in stratosphere
N ₂ O	2.5 x 10 ⁻⁷	Dissociates in stratosphere
H ₂	5 x 10 ⁻⁷	Dissociates in thermosphere
CO	5 x 10 ⁻⁸	Variable, industrial as well as atmospheric origin
NO.NO ₂	5 x 10 ⁻¹⁰ to 2 x 10 ⁻⁸)	

Table I, from the data of Nicolet (2), shows the principal and trace constituents of the atmosphere. A cursory examination of this table reveals that although the atmosphere contains large quantities of oxygen and is, therefore, an oxidizing atmosphere, it also contains appreciable quantities of gases which are characteristic of reducing atmospheres, namely, CH₄, CO and H₂. The simultaneous presence of methane and oxygen can only, it is believed, be explained on the grounds that a terrestrial biota exists. The observed concentrations of CO and H₂ may also be indicative of the presence of life, as may that of N₂O. The arguments supporting the contention that these constituents have biological import are outlined below.

METHANE

The strongest atmospheric evidence for a terrestrial biota is atmospheric methane, which is present to the extent of 1.5 parts per million. Although methane is unique among hydrocarbons in its stability and reluctance to react with O₂ and other oxidizing gases in the lower atmosphere, it nevertheless cannot persist indefinitely. Methane will oxidize at stratospheric levels by reaction with atomic oxygen (5) (6). The identity of the final products of methane oxidation is not clear; the most probable first step appears to be



The methylene radical is highly reactive and could undergo further oxidation leading to most or all of the following stable final products: H₂O, CO₂, CO, and H₂.

Although the details of the fate of methane in the atmosphere may be obscure, there can be no doubt that it is oxidized and that its oxidation is an irreversible process. The converse reaction leading to the formation of methane in the atmosphere is highly improbable. To form methane from the carbon and hydrogen compounds of the atmosphere requires a sequence of reactions involving at least four steps. The intermediate compounds in the sequence towards methane must all be partially oxidized organic compounds or free radicals. The probability that any of these, once formed, will encounter the rare molecule necessary for the next step before reaction with the abundant oxygen or decomposition by UV radiation is vanishingly small. The probability that all four sequential steps will occur is, therefore, virtually zero. For these reasons the oxidation of methane in the atmosphere may be concluded to be irreversible. The presence of methane, therefore, implies that it is being produced at the surface, but the arguments against its abiological production in the atmosphere also apply to the likelihood of its abiological production at the surface. Although it is conceivable that some methane can be abiologically produced at the surface, for example by reaction of iron carbides with water, this would be very rare and could not possibly be expected even to give rise to atmospheric concentrations many orders less than exist. Even if, for example, the oxidation of methane were so slow as to result in a residence time of 10⁶ years, the corresponding production rate required to maintain the current concentration would have to be 10⁶ molecules cm⁻² sec⁻¹.

Methane can, of course, be produced in a reducing atmosphere at high temperatures and there now seems little doubt that methane was at one time a major constituent of the early terrestrial reducing atmosphere. Methane could not have persisted in the atmosphere during its transformation to an oxidizing atmosphere, nor could it have remained isolated from the atmosphere during the long period since oxygen became a primary constituent, now to reappear as an outgassed product. Methane could not survive the temperature, pressure and chemical conditions deep in the Earth. This does not necessarily apply to Mars or other planets, where, so far as is known, temperature and pressure conditions within the planet may not be comparable with those of Earth. Of course, if the atmosphere of Mars is a reducing one, as now seems likely, the presence of methane as a constituent cannot necessarily be invoked in support of the hypothesis of its biological genesis, unless it is known that the UV flux on Mars is sufficient for its rapid removal and the prevailing surface conditions preclude its abiological replacement.

OXYGEN

The fact that 20 per cent v. of the Earth's atmosphere is oxygen is not, in itself, conclusive evidence that life exists, although many, in attempting to account for this concentration, have argued an important biological role from the known photosynthetic production of oxygen (see, for example (3) and (10)). These arguments may be countered by the observation that biotic consumption of respiratory oxygen may account for all that is photosynthetically liberated, so that the total available quantity is not influenced by the biota.

The biological significance of oxygen does not lie in its current abundance, but in the discrepancy between its probable rate of abiological production in the atmosphere and the rate at which it is apparently removed from the atmosphere.

That the terrestrial atmosphere was at one time a reducing atmosphere seems well established, but the nature of the mechanisms responsible for the loss of hydrogen and the consequent transformation to an oxidizing atmosphere is uncertain. Photolytic decomposition of H_2O with escape of the hydrogen undoubtedly played a significant role in this transformation, although there is disagreement as to its extent. (A good survey of this controversy, up to 1954, is presented by Hutchinson (4).) The disagreement is not important. The fact is that this is the only abiological mechanism offered to account for the loss of hydrogen and the release of O_2 . This process is still going on, though at a lower rate than during the early history of the Earth, because the high concentration of O_2 limits the efficiency of the photolytic process. The present estimate, based on a current loss of 2.5×10^7 atoms of hydrogen $cm^{-2} sec^{-1}$ corresponds to a total oxygen production of approximately 1.2×10^7 atoms $cm^{-2} sec^{-1}$ (2). It is clear that any evidence which supports the conclusion that oxygen is being removed much more rapidly from the atmosphere than it is photolytically produced requires an additional oxygen production mechanism.

In the preceding section the presence of methane was shown to imply a biological methane production mechanism, on the grounds that methane and oxygen are incompatible. It also implies a consumption of oxygen, since oxygen reacts with methane to form oxides of carbon and hydrogen. The lifetime of methane is very long in the lower atmosphere, but above the tropopause it is oxidized by O and HO₂. Table II, from Bates & Nicolet (6), shows the lifetime of methane towards oxidation by O in the stratosphere in the region from 30 to 50 km. Above 70 km the lifetime is much shorter (5). Consequently the rate of oxidation of methane is dependent on the speed with which it is transported to regions above about 30 km, which is accomplished by diffusion and by large scale motions of the atmosphere, the latter being the more effective. Since the characteristic times associated with these motions are not known, a realistic estimate of the methane oxidation rate cannot be made. However, it seems unlikely that these motions could be so slow as to result in a methane residence time of more than 1000 years. This conclusion is supported by the fact that the C¹⁴ activity of atmospheric methane is close to that of atmospheric CO₂. The abundance of methane is approximately 3.2×10^{19} molecules per square cm. atmosphere column. A 1000-year residence time, therefore, corresponds to an oxidation rate on the order of 10^9 molecules cm⁻² sec⁻¹, which implies a consumption of not less than three times as many oxygen atoms, assuming that the final reaction products are CO and H₂O. The observed concentration of methane and the assumption that its residence time is not greater than 1000 years therefore lead to the conclusion that oxygen must be produced at a rate not less than about 100 times that estimated for photolytic decomposition.

TABLE II

The lifetime of methane toward oxidation by monatomic oxygen, from the data of Bates & Nicolet (6).

Altitude (km)	Lifetime (sec)
30	1×10^8
40	2×10^6
50	3×10^5

Unless the rate of photolytic decomposition of H₂O has been very seriously underestimated, these considerations imply that there must be additional sources of atmospheric oxygen. We conclude that these sources are probably biological in nature because aeronomists have failed to postulate alternative abiological oxygen production processes to account for the transition from reducing to oxidizing conditions.

The fact that oxygen is being temporarily removed from the atmosphere at a greater rate than it is abiotically produced does not support the conclusion that the terrestrial biota is responsible for a net increment in the

supply of O_2 . The oxygen produced by the biota is consumed in the oxidation of biotic products. We are not concerned here with the origin of the atmosphere nor with the details of the biological mechanisms which govern oxygen concentration, but with the fact that the present atmosphere is evidence of a present biota.

CARBON MONOXIDE, HYDROGEN AND NITROUS OXIDE

CO and H_2 are gases which are characteristic of a reducing atmosphere. Their mere presence in an oxidizing atmosphere is, therefore, suggestive. But they do not provide good evidence for life, because they are the products of reversible dissociation reactions involving other constituents of the atmosphere, H_2O , CO_2 and oxygen. This means that, in all probability, these gases will always be present in certain amounts in atmospheres containing the former compounds, as a consequence of abiological processes. The critical question is whether the observed concentrations can be accounted for on this basis or whether they are excessive.

The relevant aeronomical arguments are involved and inconclusive. Both CO and H_2 are produced in the upper atmosphere by photodissociation of CO_2 and H_2O . To estimate the rate of production the concentrations of the parent molecules must be known, together with the rates at which these are replenished in the production zone by the relevant atmospheric transport mechanisms. Both CO and H_2 are removed by oxidation in regions below their production zones, the rates of removal in these being dependent upon the physical and chemical conditions and, in particular, on the concentrations of the relevant reactive molecular species such as OH , HO_2 and O and on the temperature and pressure. The over-all oxidation rate is clearly dependent, in addition, upon the rate at which CO and H_2 are transported downward to the removal zones. Without fairly accurate information on which to base estimates of turnover rates, the concentrations which would be expected under abiological conditions cannot be specified. At present, such information is lacking, especially in regard to vertical transport phenomena. It is, therefore, not possible to arrive at firm estimates of the abiological steady state concentrations of CO and H_2 .

In spite of these uncertainties, the concentration of CO appears to be somewhat excessive. Bates & Witherspoon (5) report that the observed concentration of CO is difficult to account for solely in terms of upper atmosphere photo-dissociation of CO_2 . Similarly, the analyses of Hesstvedt (11) indicate the difficulty of accounting for the abundance of hydrogen in terms of its downward transport from the region of its photochemical production.

N_2O also appears to be a somewhat anomalous constituent, but not because of any inconsistency about its presence in an oxidizing atmosphere. The possible biological significance of N_2O is that its lifetime in the atmosphere is short because it is readily destroyed by comparatively long-wavelength UV radiation. Goody & Walshaw (7) calculated the removal rate to be in the order of 10^{11} molecules cm^{-2} sec^{-1} . Several authors (8) (9) have considered possible abiological atmospheric reactions capable of generating N_2O and it is

not yet clear whether any of these reactions can account for a production at the required level. All of the proposed production reactions take place in the stratosphere or higher.

The question of the biotic significance of these gases (and possibly others) could perhaps be decided if information about their abundance profiles were available. These profiles would aid in determining where the gas is produced and where it is removed. The significance of an abundance profile may be illustrated by a highly simplified example of a hypothetical compound AO which is assumed to photolyse in the upper atmosphere to $A + O$. It is also assumed that the reverse reaction will occur readily with oxygen atoms, but not with O_2 . The atmosphere can be divided into four principal regions: an upper region where photolysis is complete; the next highest region where A can recombine with oxygen atoms; a transport zone; and the lowest region where A is uniformly distributed and where no atmospheric reactions occur. Figure 1 shows these regions together with three hypothetical abundance profiles. If substance A is neither produced nor removed at the surface, there will be no change in concentration below the recombination zone and its abundance profile will resemble profile 1. If, however, the substance is produced at the surface, its profile will resemble 2, which shows a concentration in the lower atmosphere exceeding that in the transport zone. The converse will be true of substances which are removed at the surface and which show a concentration minimum in the mixed zone, see profile 3.

The biotic significance of surface production and removal reactions of Earth is that the portion of the solar flux capable of effecting chemical reactions among the constituents of the atmosphere does not reach the surface of Earth. Consequently, any chemical reactions occurring at the surface capable of maintaining detectable concentration gradients like profile 2 or 3 in Figure 1 can only be attributed to the action of a biota. Continuing chemical reactions between the atmosphere and the solid surface are prevented by the extreme slowness of diffusion processes in the solid state. Even a liquid surface such as the sea will be characterized by relatively slow chemical reactions and, under abiological conditions, its surface layers should be in equilibrium with the atmosphere. On Earth, diffusion of gases from below the surface is quantitatively insignificant and hence incapable of maintaining concentration gradients that could be confused with those indicative of life processes.

REVIEW OF EVIDENCE

In the preceding sections an attempt has been made to demonstrate the existence of a terrestrial biota from evidence consisting wholly or largely of the composition of the atmosphere. The significance of this demonstration lies in the possibility of drawing comparable biological inferences from information about the atmospheres of other planets. It is, therefore, useful to review the kinds of information used above to support these conclusions.

The first and strongest argument is that based on the observation of atmospheric methane, which undergoes irreversible reaction with oxygen, in

conjunction with a large concentration of atmospheric O_2 . It is a chemical argument which requires almost no knowledge of atmospheric physics for its validity. If the concentrations of either methane or oxygen were less than they are, the argument would still hold.

The second argument is also based on the observation of methane and oxygen, but requires, in addition, an assumption about the effects of large scale movements of the atmosphere in transporting methane, together with estimates of the rate of photolytic production of oxygen and of the lifetime of methane in the stratosphere. These two estimates are derived from fairly detailed and sophisticated models of the atmosphere and, implicit in them, fairly detailed knowledge of its physical structure. To the extent that the second argument implies far more knowledge of atmospheric processes, it is much weaker than the first. If methane were less abundant, the second argument could not be supported.

The last three constituents considered, CO , H_2 , and N_2O , do not provide unequivocal evidence of life; they are just suggestive. The biological significance these constituents can now be said to have seems to depend almost entirely upon rather sophisticated and involved aeronomical reasoning for the details of which the reader is referred to the literature already cited. If additional atmospheric measurements in the form of concentration profiles of CH_4 , CO , H_2 and N_2O were available, much of the ambiguity might be removed.

Some of the inconclusiveness of aeronomical arguments may be due in part to the fact that aeronomists need not base conclusions about the origin of atmospheric gases on atmospheric measurements alone. In the case of the Earth, at least, there is considerable information on the production of atmospheric "contaminants" by the biota. In Table III some recent estimates are given of the biotic production of some of the gases considered above, together with their atmospheric abundance.

BIOLOGICAL SIGNIFICANCE OF EXTRATERRESTRIAL ATMOSPHERIC ANALYSES

The object of this inquiry into the biological significance of the terrestrial atmosphere has been to determine whether analysis of the atmosphere could be viewed as a life detection experiment, with particular reference to Mars. The following conclusions seem to follow from the preceding discussion:

1. Not only is the presence of a terrestrial biota reflected in the composition of the atmosphere; it can also be inferred almost entirely from atmospheric measurements alone. In particular, no assumptions about the nature and biochemistry of the biota are necessary for such an interpretation.
2. The biological significance of an atmospheric mixture lies in the relative concentrations of a variety of constituents and not wholly in the presence or absence of any single one of them. Such a mixture is biologically significant if it represents a departure from a predictable abiological steady state. The strongest evidence is the simultaneous presence of two gases, like methane and oxygen, capable of undergoing

irreversible reaction; even with gases which can be expected to occur under abiological conditions, departures from the abundances to be anticipated will be of biological significance.

3. The presence of even very minor constituents may be very significant; consequently, every attempt should be made to provide as complete an analysis of the atmosphere as possible.

TABLE III

Estimated abiological and biological production of selected atmospheric components contrasted with atmospheric abundance.

Gas	Atmospheric Abundance Molecules cm ⁻² column	Abiological Production Molecules cm ⁻² yr ⁻¹	Biological Production Molecules cm ⁻² yr ⁻¹
Oxygen	4.5 x 10 ²⁴	1.9 x 10 ¹⁷ (2)	3.2 x 10 ²⁰ (13)
Carbon Dioxide	6.4 x 10 ²¹	-	3.2 x 10 ²⁰ (13)
Methane	3.2 x 10 ¹⁹	nil	2 x 10 ¹⁸ (12)
Hydrogen	1.0 x 10 ¹⁹	-	1.0 x 10 ¹⁵ (12)*
Nitrous Oxide	5.0 x 10 ¹⁸	1.0 x 10 ¹⁶ to 1.0 x 10 ¹³ (7) (8)	5.0 x 10 ¹⁷ (7)
Carbon Monoxide	1.0 x 10 ¹³	1.0 x 10 ¹⁶ (5)	8.0 x 10 ¹⁷ (5)

* Does not include hydrogen of industrial origin.

By analogy with Earth, Martian life, if present, may affect Mars' atmosphere by giving rise to anomalous concentrations of compounds whose presence could be expected as a result of abiological reactions and/or by concentration in the atmosphere of compounds incompatible with other constituents.

Life detection by atmospheric analysis might be argued to be more appropriate to planets which, like the Earth, have a high density of living matter at or near the surface, but inapplicable to planets on which the biota, if present, is likely to be very thin. But the ratio of atmospheric mass to surface area is 30 times less for Mars than for Earth, so that the quantity of living matter required to produce comparable effects could be much less. Furthermore, the removal of one biologically produced component could, conceivably, be dependent upon the simultaneous presence of another similarly

produced. If the removal rate is concentration dependent, an easily measured steady state concentration can occur even when the production rate is very low. A more fundamental point is that the ability of a biota to control its environment and drive it to a state of low entropy is not a function of the density of that biota; it follows from the tendency of living organisms to continue to grow and develop until the supply of available raw materials establishes a limit. Consequently, the detectability of a planetary biota by means of atmospheric compositional analysis is not necessarily limited by the density of the biota.

A life detection experiment based on analysis of the Martian atmosphere should be designed to measure the concentrations of as many of the components of the atmosphere as possible, including both the major and the trace components. In view of what is not known of the Martian atmosphere or surface, it would be unwise at this stage to prejudice the experiment by guessing what may be the more significant constituents to measure. The significance of any single compound can only be determined after the analytical information has been obtained and interpreted. This requires at least a minimum of supporting information to make possible the specification of the conditions under which these components would be expected to react. Some of this auxiliary information, such as the solar spectrum and the temperature at the surface, are already available; the state of oxidation of the surface and the radiation flux at the surface may be available during the early Voyager missions. This latter information may not be necessary for the unequivocal interpretation of the biological significance of the atmospheric measurements, but they would be of value in confirming any conclusions. If, as is possible, the Martian atmosphere is poised between an oxidizing and a reducing state, knowledge of the oxidation state of the surface would be of great value.

Information regarding isotopic concentrations may also be of importance. In particular, where the same element occurs in two or more atmospheric compounds, the relative amounts of its isotopes would provide valuable information on the nature of the reactions between them. The well known ability of living organisms to fractionate isotopes of the same elements provides a means of distinguishing biotic and abiotic reactions; thus, evidence of clear isotopic selectivity might in some circumstances be suggestive evidence of biotic transformation.

CONCLUSION

Science is divided artificially into a spectrum of disciplines ranging from Physics to Biology. The language, thought, and experimental approaches of each has been conditioned by the historical course of their development and by the nature of the experimental evidence available for consideration. It is inevitable that Biology and associated disciplines such as Biochemistry are geocentric in nature if only because of the lack of any experimental experience other than that on Earth. By a similar process of development that branch of Physics dealing with astronomy is essentially exocentric in approach, even to the point of a blindness to biological phenomena at the Earth's surface.

Hitherto almost all experiments proposed for extra-terrestrial life detection have arisen from an essentially biological background and have sought to recognize life elsewhere in terms of well known laboratory procedures on Earth such as micro-biological growth experiments and the analytical procedures of biochemistry. Apart from the overwhelming geocentric bias of these approaches, the mechanics of transporting a biochemical laboratory to another planet are expensive and technically of the greatest difficulty. The purpose of this paper has been to draw attention to the obvious fact that the phenomenon of life is not arbitrarily limited to effects occurring in the realm of "Life Sciences." Because of this the presence of life on other planets may be recognized from comparatively simple measurements of their physical environment and superficial chemical composition. Such measurements may even be possible by astronomical observations from the Earth and, if successful, would serve to guide the more detailed understanding of their nature by the more complex approaches such as those of the biological sciences.

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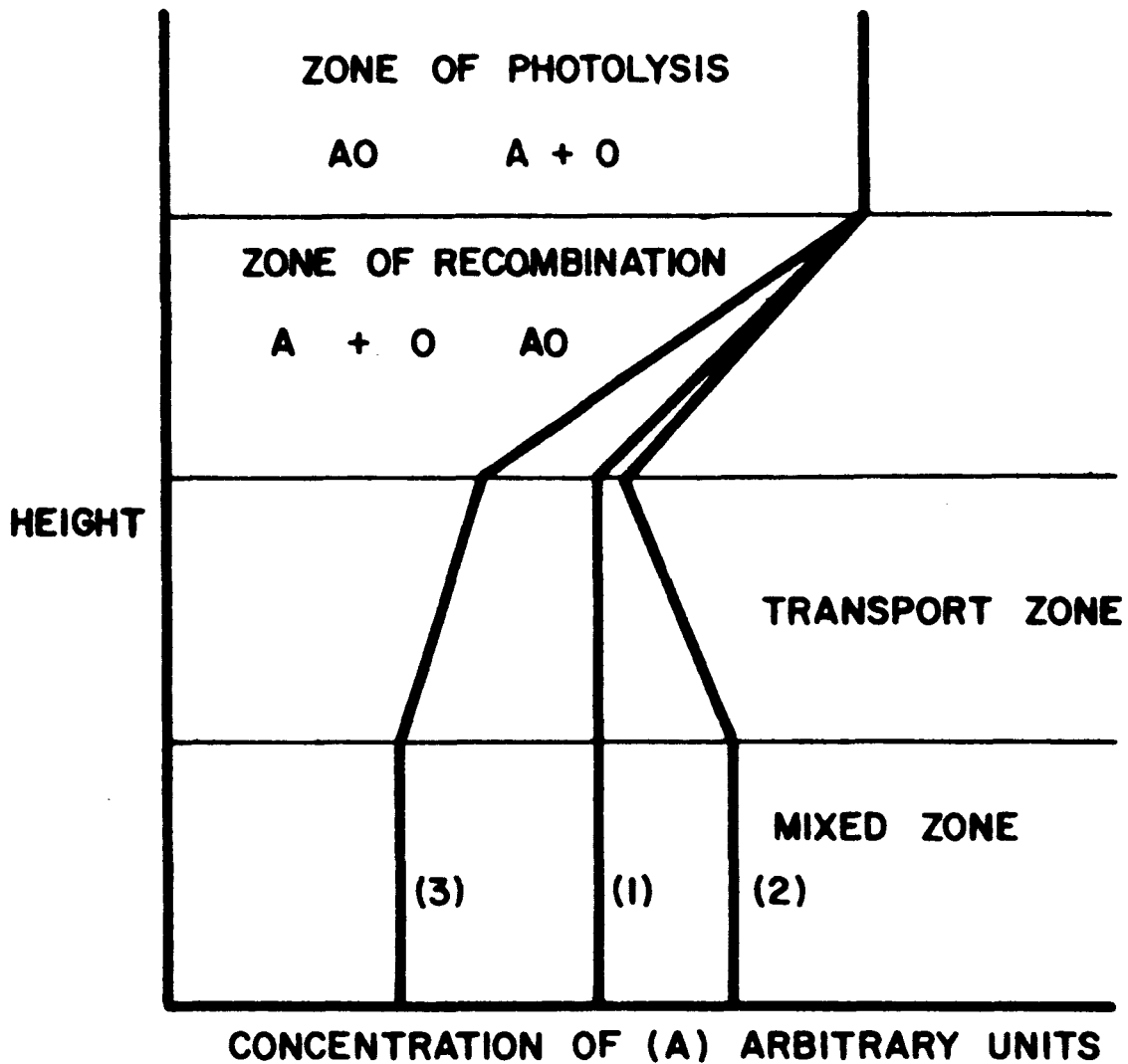


FIGURE 1

Atmospheric distribution of a hypothetical molecule (A) the product of the photochemical dissociation of the oxide (AO) in the upper atmosphere.
 (1) No reaction at the surface (2) Production at the surface (3) Removal at the surface.

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