

the mass defect information contained in the descent data in the hope that we might be able to better identify the atmospheric constituents.

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15 May 1979

Laboratory Corroboration of the Pioneer Venus

Gas Chromatograph Analyses

Abstract. *Laboratory simulation and tests of the inlet sampling system and columns of the Pioneer Venus gas chromatograph show that the sensitivity to argon is not diminished after the column regeneration step, argon isotopes are not separated, oxygen and sulfur dioxide are not produced in the inlet sampling system from sulfur trioxide, and sulfur trioxide is not formed from sulfur dioxide and oxygen. Comparisons of the volatile inventory of Venus and Earth imply similar efficiencies of early outgassing but a lower efficiency for later outgassing in the case of Venus. The high oxidation state of the Venus atmosphere in the region of cloud formation may prohibit the generation of elemental sulfur particles.*

We reported earlier on the composition of the Venus lower atmosphere as analyzed by the Pioneer Venus gas chromatograph (PVC) (1). A number of apparent discrepant data have been reported between the compositional analyses about an assumed well-mixed lower atmosphere from in situ as well as extrapolated data from the upper atmosphere (2). The accuracy of compositional data is critical for testing the validity of or for evolving working hypotheses about the origin, evolution, and dynamics of planetary atmospheres and the nature of clouds, and will provide clues to an understanding of the origin and evolution of the planets in our solar system.

We are currently scrutinizing and testing in detail our analytical findings to evaluate these disparities. This report is

concerned primarily with some of the completed studies on the backup laboratory simulations for assessing the reliability and validity of the flight data and secondarily with general conclusions about the significance of the corroborated data.

In examining the estimation for total Ar, we have had two concerns. (i) Did the procedure for regeneration of the columns, which was sequenced to improve sensitivity to O₂ and SO₂ prior to entry, reduce the sensitivity for Ar? (ii) Was the O₂ peak misidentified as ³⁶Ar because the column actually separated ³⁶Ar from ⁴⁰Ar?

To answer the first question, we subjected an identical column of Porapak N to the exact sequence of valve operations that occurred in the flight regenera-

tion procedure. The regeneration sequence admitted a gas mixture of O₂ and SO₂ in He (1 percent by volume each), and then the column was purged with He. A calibration gas mixture containing ~ 500 parts per million (ppm) each of H₂, O₂, Ne, CO, N₂, and Ar in He was injected prior to the regeneration cycle and after it at times corresponding to the three altitudinal sampling times on the mission.

Table 1 shows the ratios of responses obtained before and after regeneration. The ratios, without exception, show that at least within the 3 σ confidence interval (σ is the standard deviation), 90 percent of each sample gas response is retrievable. Thus the analyses for Ne, N₂, O₂, and Ar are not significantly changed.

Deliberate isotopic separations in gas chromatography are attainable at very low temperatures, and we assumed that at the temperatures we chose to regulate our flight columns ³⁶Ar/⁴⁰Ar separations did not occur. We did not run these tests prior to flight since we did not have available an enriched source of ³⁶Ar. However, the differences in the mass spectrometric data (2) by comparison with the gas chromatographic data suggested that perhaps the misidentification of O₂ for ³⁶Ar could account for some of this disparity. That this did not actually occur is fortified by our laboratory data.

Mass spectrometric analyses (3) of a gas mixture containing roughly equal parts of ³⁶Ar, ³⁸Ar, and ⁴⁰Ar (4) showed the responses listed in Table 2. In the gas chromatography of this mixture we used a Porapak N column; the chromatogram exhibited a single large peak (Ar) and two smaller peaks identified as N₂ and CO (Fig. 1), demonstrating the inseparability of the three Ar isotopes. The O₂ peak retention time is between the N₂ and the Ar peak. In addition, the chromatogram demonstrates that O₂ in the flight data is not misidentified and is a real constituent of the Venus atmosphere in the sample loop.

The next question that we addressed was whether any part of the O₂ could have been derived from the thermal or catalytic breakdown of SO₃ in the inlet system. Concern for this possibility arises from the fact that 1 mole of SO₃ could thermally degrade to 1 mole of SO₂ and 1/2 mole of O₂ (5); our data show a ratio of exactly 2.68/1 for SO₂/O₂ for both the second and third samples in which both components were measurable.

When SO₃ was passed through a simulated inlet system at different temperatures, no significant release of O₂ and SO₂ occurred (Table 3). Thus any SO₃ component and ostensibly H₂SO₄ in the Venus atmosphere would not be dis-

Table 1. Response characteristics for selected gases during the analytical sequence of the simulated flight.

Sample	Fraction of calibration response				
	Ne	N ₂	O ₂	Ar	CO
1	0.99 ± 0.03	0.99 ± 0.04	0.89 ± 0.04	0.92 ± 0.04	0.87 ± 0.05
2	0.95 ± 0.04	1.02 ± 0.06	0.94 ± 0.04	0.90 ± 0.05	0.94 ± 0.08
3	1.00 ± 0.03	0.98 ± 0.04	0.96 ± 0.04	0.98 ± 0.04	1.03 ± 0.05

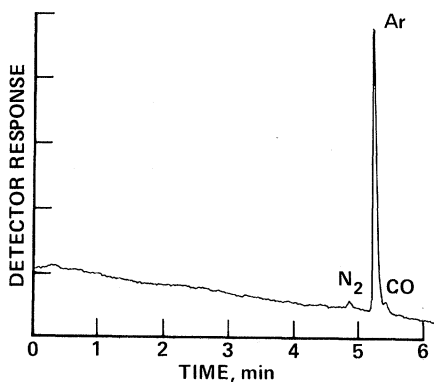


Fig. 1. The gas chromatogram of a gas mixture containing roughly equal amounts of ^{36}Ar , ^{38}Ar , and ^{40}Ar and traces of N_2 and CO . The chromatography was carried out on a Porapak N column similar in dimensions and conditions to that in the PVGC.

sociated at 170°C (the highest temperature attained in the sampling system) in the residence time allowed by the flow rate through the sampling system.

The reverse reaction, the combination of SO_2 and O_2 to form SO_3 , was also tested in the same system. Using premixed SO_2 and O_2 through the simulated sampling system, we observed no significant alteration of the composition until temperatures in excess of 475°C were attained (Table 4). These data show that SO_2 and O_2 as measured by the PVGC are accurately representative of the actual atmosphere of Venus. There is no contribution from SO_3 to the SO_2 and O_2 if SO_3 exists as such in the Venus atmosphere at the sampling altitudinal swaths. Nor is there any significant loss of SO_2 and O_2 to the synthesis of SO_3 in the inlet system.

The Pioneer Venus gas chromatograms containing peaks for Ne, N_2 , O_2 , and Ar were obtained from a given sample, a single column, and a detector in series with that column. If the analyses for Ne and total Ar were in error by five to ten times, as implied by the mass spectrometric data, a corresponding multiple increase for N_2 would be indicated. The N_2 content would thus be increased from 3.4 percent to the range 17 to 34 percent, a highly implausible value in view of the nearly exact correspondence of the N_2 mass in respect to planet mass for Venus and Earth that is obtained for the 3.4 percent measurement (1).

Some other conclusions have also been reached. The ratio of the mass of outgassed radiogenic argon (^{40}Ar) to the mass of Venus is smaller by about a factor of 15 than the value for Earth, despite the fact that the mass ratios for outgassed N_2 and CO_2 are essentially the same for the two planets (1, 6). These comparisons can be understood in terms

of a two-component model of outgassing: Planets may undergo extensive melting and outgassing in their early history, and a more episodic and localized melting and outgassing may occur throughout the remainder of their lifetimes (6). Since ^{40}Ar is created continuously over time within a planet's interior as a result of the radioactive decay of ^{40}K , its abundance in the atmosphere reflects primarily the efficiency of the second stage of outgassing; all the other volatiles can be released during the first epoch of outgassing. Thus, the comparable amounts of outgassed N_2 and CO_2 for Venus and Earth imply comparable degrees of outgassing during the early epoch, whereas the smaller amount of ^{40}Ar for Venus implies a less efficient outgassing for that planet during later epochs (6). Venus may have a less efficient stage of later outgassing because of the more plastic behavior of the near-surface rocks due to the high surface temperature which may inhibit fracturing (6) and a greater retentiveness of rare gases by the near-surface material due to the anhydrous environment (7) as implied by the great depletion of water in the Venus atmosphere relative to the amount in the oceans of Earth (1).

Our measurements indicate that the

Table 2. Isotope analysis of the Ar mixture.

Mass	Back-ground (V)	Sample (V)	Net (V)	Identification
12	0.001	0.013	0.012	C^+
14	0.001	0.005	0.004	N^+
16	0.002	0.022	0.020	O^+
17	0.012	0.026	0.014	OH^+
18	0.049	0.21	0.16	H_2O^+ , $^{36}\text{Ar}^{2+}$
19	0.001	0.14	0.14	$^{38}\text{Ar}^{2+}$
20	< 0.001	0.15	0.15	$^{40}\text{Ar}^{2+}$
28	0.065	0.86	0.80	CO^+ , N_2^+
32	0.002	0.004	0.002	O_2^+
36	0.002	2.19	2.19	$^{36}\text{Ar}^+$
38	< 0.001	1.93	1.93	$^{38}\text{Ar}^+$
40	0.001	2.02	2.02	$^{40}\text{Ar}^+$

Table 3. The stability of SO_3 in the simulated inlet sampling system of the PVGC. A 1.6-m length of 316 stainless steel tubing (0.058 cm in inside diameter) served as a simulator for the inlet system of the gas chromatograph. The flow of He gas over 30 percent SO_3 in concentrated H_2SO_4 was maintained at $1.6 \text{ cm}^3 \text{ min}^{-1}$, which equates to a linear flow of $\sim 10 \text{ cm sec}^{-1}$ through the tubing.

System temperature ($^\circ\text{C}$)	Detector response for	
	O_2 (μV)	SO_2 (μV)
25	0	8
160	0	8
280	0	3
475	4	12

Table 4. The stability of SO_2 and O_2 individually in the simulated inlet sampling system of the PVGC.

System temperature ($^\circ\text{C}$)	Peak height detector response for	
	O_2	SO_2
<i>SO_2/O_2 ratio = 10</i>		
25	57.4 mV	3.44 mV
25	57.2 mV	3.44 mV
120	56.4 mV	3.48 mV
150	57.2 mV	3.44 mV
185	58.8 mV	3.44 mV
250	58.8 mV	3.44 mV
425	56.8 mV	3.54 mV
525	56.4 mV	3.48 mV
<i>SO_2/O_2 ratio = 1</i>		
25	4080 μV	396 μV
25	4100 μV	396 μV
140	3910 μV	388 μV
155	4090 μV	396 μV
195	4140 μV	
200	4130 μV	
325	4130 μV	398 μV
340	4050 μV	398 μV
460	3980 μV	398 μV
480	4050 μV	398 μV
525	3870 μV	386 μV
530	3790 μV	384 μV

Venus atmosphere is an oxidizing rather than a reducing state in the region where the main cloud material is generated (1). Thus, SO_2 appears to be the dominant sulfur-containing gas in this region ($\sim 180 \text{ ppm}$) and free O_2 is present in significant amounts ($\sim 70 \text{ ppm}$), whereas there seem to be very stringent upper limits on the concentrations of CO ($\leq 0.6 \text{ ppm}$) and COS ($\leq 2 \text{ ppm}$). These chemical properties of the Venus atmosphere make it extremely difficult to generate elemental sulfur particles either by gas-phase photochemistry near the cloud tops or by thermochemistry near their bottoms (8). Since sulfur has been advocated as a cloud constituent in an effort to explain the low reflectivity of Venus in the near-ultraviolet (UV) region and the occurrence of spatial contrast in this domain (9), alternative sources of UV absorption need to be investigated (10). Preliminary comparisons between the observed behavior of Venus and that predicted by a number of proposed UV absorbers indicate that SO_2 gas may be the UV absorber (10).

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4. W. Rison, Department of Physics, University of California at Berkeley, supplied us with the Ar gas mixture.
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15 May 1979

Venus Upper Atmosphere Neutral Gas Composition: First Observations of the Diurnal Variations

Abstract. *Measurements of the composition, temperature, and diurnal variations of the major neutral constituents in the thermosphere of Venus are being made with a quadrupole mass spectrometer on the Pioneer Venus orbiter. Concentrations of carbon dioxide, carbon monoxide, molecular nitrogen, atomic oxygen, and helium are presented, in addition to an empirical model of the data. The concentrations of the heavy gases, carbon dioxide, carbon monoxide, and molecular nitrogen, rapidly decrease from the evening terminator toward the nightside; the concentration of atomic oxygen remains nearly constant and the helium concentration increases, an indication of a nightside bulge. The kinetic temperature inferred from scale heights drops rapidly from 230 K at the terminator to 130 K at a solar zenith angle of 120° , and to 112 K at the antisolar point.*

This is the second report of preliminary results obtained from the Pioneer Venus orbiter neutral mass spectrometer (ONMS). In the first report (1) we presented data on the initial composition of the major constituents of the atmosphere near the evening terminator. Later data from more than 100 orbits covering a range of solar zenith angles (SZA) from 80° near the evening terminator to 174° near the antisolar point and to approximately 130° toward the morning terminator have been obtained.

Details of the Pioneer Venus spacecraft and the orbit parameters have been described by Colin and Hall (2) and Colin (3). The measurement techniques used to obtain ambient gas densities and kinetic temperatures with the ONMS are described in (1). We present here the first observations of the diurnal variations of the composition and temperature in the thermosphere of Venus. We discuss only average conditions with the aid of an empirical model whose parameters are obtained by a numerical fit to the data. In

contrast to the model values, the measured densities change from orbit to orbit for a given altitude; thus the atmosphere on the nightside of the planet is variable.

The preliminary global model of the Venus thermosphere we present has been developed with the same basic formalism used for the mass spectrometer and incoherent scatter model (4). Data from 60 selected orbits distributed over the range of SZA encountered, from 80° to 174° , were used. A lower bound of 130 km has been chosen, and the only independent variable is SZA. The temperature and lower-bound densities are expanded in a series of Legendre polynomials in SZA (rather than latitudes and local time). Polynomials up to order four were used for exospheric temperature, and only the first-order polynomial (P_1) was used for the lower-bound densities. Exospheric temperature was determined from a simultaneous fit of He and N_2 densities and adopted for fitting CO , CO_2 , and O. The data used were limited to heights less than 250 km for He and less than 180 km for the other gases. The lower-bound temperature was fixed at 180 K to match the infrared temperature (5), and a Bates temperature profile was chosen.

An example of the measured N_2 densities in an altitude interval from 165 to 169 km is shown in Fig. 1. The large changes from orbit to orbit illustrate the dynamic character of the atmosphere. Multiple points at a particular orbit (vertical line) are due to differences in sampling altitude and latitudinal variations (data taken during descent and ascent are presented). The solid line in Fig. 1

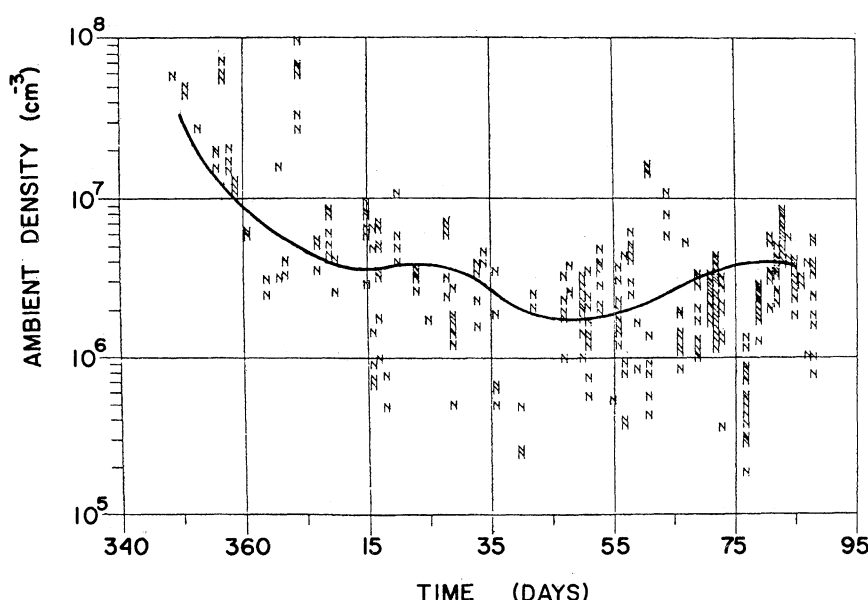


Fig. 1. Densities of N_2 versus time. Densities (N) were measured over an altitude interval from 165 to 169 km. The scatter reflects atmospheric variations and, to a small extent, altitude change. The solid line represents model values.

Table 1. Concentrations of the major atmospheric constituents at an altitude of 150 km and SZA = 180° .

Component	Density (particles per cubic centimeter)
CO_2	8.0×10^7
CO	1.7×10^7
N_2	5.0×10^7
O	4.4×10^8
He	1.3×10^7

Table 2. Heat sources for the nightside thermosphere (ergs per square centimeter per second averaged over the hemisphere). "Convective" refers to the heat carried across the terminator by the flowing gas; "compressional" refers to the heat generated by gas flowing downward.

Boundary (km)	Convective	Compressional	Conductive
120	2.6	0.52	0.017
140	0.03	0.006	0.0088