on the inlet leak and to preclude condensation. About 10 minutes after the probe passed out of the cloud layer the overcoating of the primary leak evaporated, aided no doubt by the heater, thus permitting a resumption of the flow of external gases through the leak. At this time marked increases were observed in signals measured by the spectrometer at mass numbers 18, 48, and 64 amu, with somewhat smaller peaks at 17, 19, 32, 50, and 66 amu. There can be little doubt that the condensed material which blocked the inlet tube contained a compound or compounds of sulfur together with H_2O. Further work will be required in order to categorically identify the condensed material. There is no reason to reject, however, at this stage, the notion that the clouds of Venus may contain significant concentrations of hydrated H_2SO_4 (*12*).

Additional evidence for the importance of sulfur may be derived from data obtained in an essentially cloud-free region at lower altitudes. Peaks were observed in the mass spectrum at 64 and 48 amu and at other mass numbers that may be associated with radicals or compounds containing sulfur. Further analysis will be required to provide categorical identification of the more abundant sulfur compounds. It is apparent, however, that the lower atmosphere of Venus must include a significant supply of sulfur and that the relative concentrations of more abundant sulfur compounds must change appreciably with altitude. Continuing analysis of these data should provide invaluable insights into the complex chemical and photochemical processes which combine to form and maintain the planet-wide clouds of Venus.

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Venus Lower Atmospheric Composition: Analysis by Gas Chromatography

Abstract. *The first gas chromatographic analysis of the lower atmosphere of Venus is reported. Three atmospheric samples were analyzed. The third of these samples showed carbon dioxide (96.4 percent), molecular nitrogen (3.41 percent), water vapor (0.135 percent), molecular oxygen [69.3 parts per million (ppm)], argon (18.6 ppm), neon (4.31 ppm), and sulfur dioxide (186 ppm). The amounts of water vapor and sulfur dioxide detected are roughly compatible with the requirements of greenhouse models of the high surface temperature of Venus. The large positive gradient of sulfur dioxide, molecular oxygen, and water vapor from the cloud tops to their bottoms, as implied by Earth-based observations and these results, gives added support for the presence of major quantities of aqueous sulfuric acid in the clouds. A comparison of the inventory of inert gases found in the atmospheres of Venus, Earth, and Mars suggests that these components are due to outgassing from the planetary interiors.*

The lower Venus atmosphere was analyzed with a gas chromatograph (GC) onboard the Pioneer Venus sounder probe on 9 December 1978 (*1*). This report presents results obtained by the GC and a discussion of the implications of the findings.

The samples were acquired at 1856:08, 1905:38, and 1916:08 spacecraft time, corresponding to altitudes based on a predicted entry profile estimated to be 54, 44, and 24 km, respectively. The altitudinal resolutions for samples acquired are estimated to be 25, 75, and 36 m, respectively.

The compositional data obtained are shown in Table 1. The results are based upon the assumption that a substantial portion of the gases introduced into the columns emerge at the detector. Since the major gas is CO_2 (~ 96 percent), the data are not likely to be altered significantly (< 4 percent) by additions of unmeasured gases to the total.

The data show that CO_2, Ne, N_2, O_2, Ar, H_2O, and SO_2 are present in the

Table 1. Atmospheric composition of Venus as measured by the gas chromatograph.

Gas	Sample number 1	Sample number 2	Sample number 3
	*Concentration (%) ± confidence interval**		
CO_2	95.4 ± 20.1	95.9 ± 5.84	96.4 ± 1.03
N_2	4.60 ± 0.0880	3.54 ± 0.0261	3.41 ± 0.0207
H_2O	< 0.06	0.519 ± 0.0684	0.135 ± 0.0149
	*Concentration (ppm) ± confidence interval**		
O_2	59.2 ± 25.2	65.6 ± 7.32	69.3 ± 1.27
Ar	$30.3^{+46.9}_{-20.3}$	28.3 ± 13.7	18.6 ± 2.37
Ne	< 8	$10.6^{+31.6}_{-9.6}$	$4.31^{+5.54}_{-3.91}$
SO_2	< 600	176^{+2000}_{-0}	186^{+349}_{-156}
Pressure (bars)	0.698 ± 0.140	2.91 ± 0.170	17.7 ± 0.183

*Confidence intervals are calculated from the calibration data acquired during the test and are determined to 3 σ (*20*).

lower Venus atmosphere, the concentrations of all these gases being well above the detectable limits of the GC. Other gases within the purvey of this designed instrument were not demonstrated, and upper limits for their presence can be established from minimum detectable concentrations (Table 2).

Table 2. Minimum detectable concentrations of gases that can be measured by the gas chromatograph but were not found.

Gas	Sample number (ppm)*		
	1	2	3
H_2	200	70	10
CO	10	3	0.6
CH_4	40	10	0.2
Kr	40	10	0.2
N_2O†	200	70	10
C_2H_4	20	7	1
C_2H_6	20	7	1
H_2S	40	10	2
COS	40	10	2
C_3H_8	90	30	5

*Minimum concentration (in parts per million) calculated for a signal-to-noise ratio of 2.4:1 with a noise level of 1 μV. †Optimum case; may be considerably higher in some cases depending on other gas concentrations.

If the assumption is valid that the Venus atmosphere is well mixed, the most reliable and most accurate data on composition are given by sample 3, because the values are well above the levels of detectability for all gases indicated. On the other hand, with increasing altitude there is an apparent increase in the concentrations of Ne, Ar, and N_2, which is bounded by confidence intervals of 3 σ for the two samples containing detectable concentrations of Ne and the three samples of Ar but not for all three samples of N_2. Thus, we can explain the variation in concentration of Ne and Ar with increasing altitude within the uncertainties of the analysis at the lower pressures in samples 1 and 2, but we cannot peremptorily exclude the N_2 increases with altitude on this basis alone.

The overall performance of the instrument was virtually perfect. Figures 1 and 2 show the sample 3 chromatograms, which demonstrate the excellence of resolution and the comparative responses of various components in the Venus atmosphere. Freon-14 and Freon-22 were added to sample 3 as internal standards.

The results reported here, with one exception, are in reasonable agreement with compositional measurements made in the lower atmosphere of Venus by earlier Soviet Venera spacecraft (2). In particular, our determination of a mixing ratio of 3.4 percent for N_2 may be compared with a value of 1.8 ± 0.4 percent obtained by mass spectrometers onboard Venera 9 and Venera 10. The Venera instruments detected a sulfur-bearing compound, which had a mixing ratio on the order of 1000 parts per million (ppm). The GC results show that SO_2 is the dominant sulfur-containing gas. The GC value of 18.6 ppm for Ar seems to be significantly different from a value of about 200 ppm reported by the Venera mass spectrometers. Venera 9 and Venera 10 also contained a narrow-band photometer experiment designed to measure the mixing ratio of H_2O below the main clouds. The derived value of about 1000 ppm approximates the value reported here.

The compositional determinations obtained by the Pioneer Venus GC have relevance to the Venus temperature structure, its cloud system, and the origin of its atmosphere. The high surface temperature on Venus ($\sim$ 730 K) has traditionally been attributed to a greenhouse effect, whereby sunlight is more easily transmitted through its atmosphere than thermal radiation in the infrared (3). In order to raise the surface temperature by about 500 K above the temperature at which the planet radiates to space, no significant "window" regions can exist at infrared wavelengths. But CO_2, the dominant constituent of the atmosphere, is fairly transparent in several regions of the infrared and is therefore incapable, by itself, of generating the required greenhouse effect (3). Both H_2O vapor and cloud aerosols have been the leading candidates suggested as supplying the additional required infrared opacity (4). Because the atmosphere lacks any appreciable cloud particles below about 48 km (5), cloud opacity can play only a secondary role in this regard. But the amount of H_2O vapor detected by the GC is comparable to the amounts required to achieve the desired greenhouse effect (4). In addition, SO_2 is present in sufficient amounts to also contribute significantly to closing the window regions (6).

Earth-based observations and their interpretations have provided strong evidence that the upper portions of the main

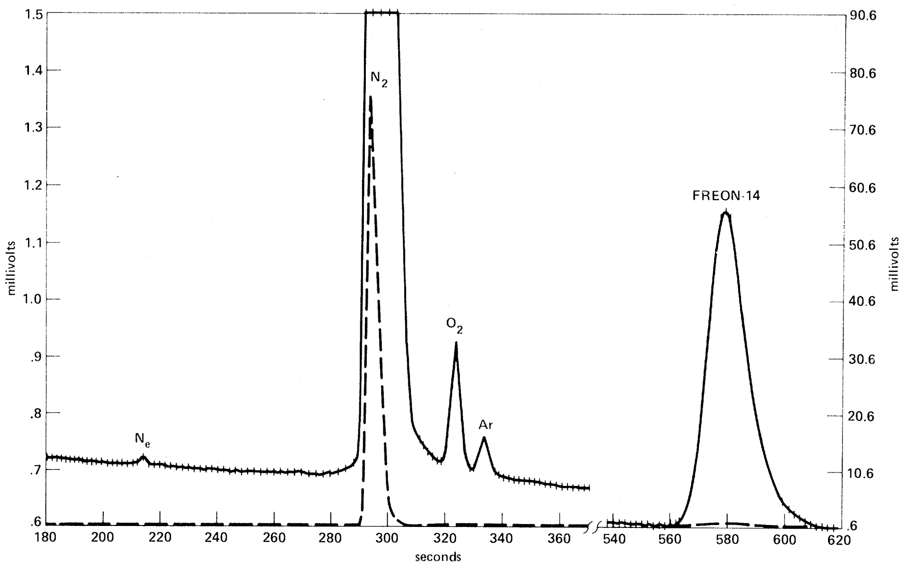

Fig. 1. Chromatogram taken with the long column of the 24-km sample, showing raw data points. The solid line shows the detector signal at a range of 0.6 to 1.5 mV. The dashed line shows the detector signal at a range of 0.6 to 90.6 mV.

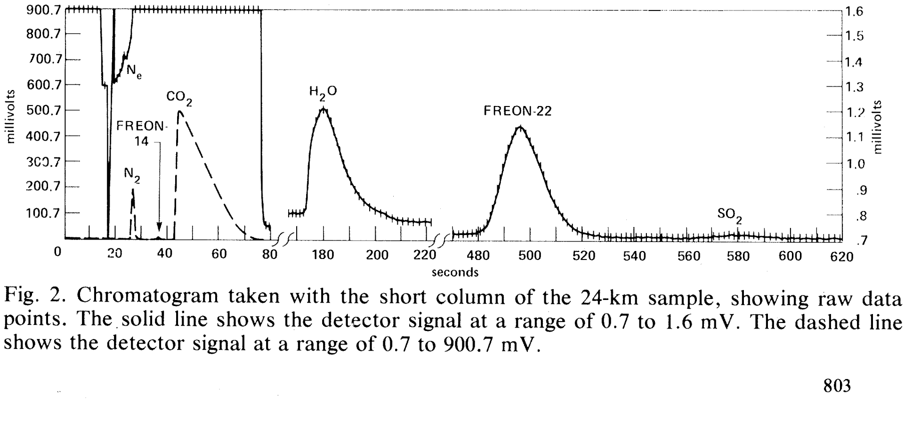

Fig. 2. Chromatogram taken with the short column of the 24-km sample, showing raw data points. The solid line shows the detector signal at a range of 0.7 to 1.6 mV. The dashed line shows the detector signal at a range of 0.7 to 900.7 mV.

Table 3. Volatile inventory of the terrestrial planets; V, Venus; E, Earth; and M, Mars.

Gas	α_i			x			r		
	V	E	M	V	E	M	V	E	M
N_2	0.034	0.78	0.027	1	~ 3	30 to 190	2.1×10^{-6}	2×10^{-6}	1.9×10^{-8} to 1.2×10^{-7}
CO_2	0.96	0.00033	0.953	1	~ 2×10^5	20 to 140	9.5×10^{-5}	7×10^{-5}	7.0×10^{-7} to 4.9×10^{-6}
H_2O	0.014	1×10^{-2}	1×10^{-3}	1	3×10^4	3×10^5 to 2×10^{-6}	5.7×10^{-8}	1.6×10^{-4}	4.5×10^{-6} to 3.2×10^{-5}
Ne	4.3×10^{-6}	1.8×10^{-5}	2.5×10^{-6}	1	1	1	1.9×10^{-10}	1.1×10^{-11}	4.2×10^{-14}
Non-R Ar*	9×10^{-6}	4.0×10^{-5}	6.0×10^{-6}	1	1	1	8.1×10^{-10}	4.6×10^{-11}	2.2×10^{-13}
R Ar*	9×10^{-6}	9.3×10^{-3}	1.6×10^{-2}	1	1	1	8.1×10^{-10}	1.1×10^{-8}	5.4×10^{-10}

*Non-R Ar and R Ar mean nonradiogenic and radiogenic Ar (from ^{40}K decay), respectively. In the case of Venus we have assumed a 1/1 ratio of these components in deriving the α_i values, in accord with the Pioneer Venus mass spectrometer results (*21*).

cloud layer are composed of a water solution of H_2SO_4 (*7, 8*), with the concentration about 85 percent H_2SO_4 (by weight). The GC results are consistent with this identification. In particular, in the region near the cloud tops, the H_2O vapor, O_2, and SO_2 mixing ratios have values of 0.5 to 40, < 1, and 0.1 ppm, respectively (*9*). Below the main clouds, the corresponding mixing ratios are about 1300, 70, and 180 ppm, respectively, according to the GC measurements. This sharp gradient in the mixing ratios through the main cloud layer can, in part, be attributed to the removal of these gases and to the formation of aqueous H_2SO_4 particles by means of photochemical processes (*10*). Below the clouds the aqueous H_2SO_4 particles evaporate first into H_2SO_4 and H_2O gases; H_2SO_4 subsequently decomposes to SO_2, O_2, and H_2O.

A somewhat surprising result of the GC measurements is that SO_2 and not COS, as had been previously conjectured (*10*), is the dominant sulfur-bearing compound in the lower atmosphere of Venus. The prior, widespread belief that there was an abundance of COS below the clouds can be traced to Lewis' hypothesis (*11*) that the CO abundance in the atmosphere is buffered by certain minerals at the surface and therefore the amount of CO detected above the clouds—about 50 ppm (*12*)—is representative of the amount below the clouds. But the GC measurements imply an upper bound of only about 0.6 ppm near an altitude of 24 km. Therefore, CO is generated almost entirely by photochemical processes and no significant amounts of COS should be expected.

The occurrence of significant amounts of O_2 in the lower atmosphere implies a higher oxidation state for the current atmosphere than it probably had originally. Alteration of the oxidation state has probably occurred over geological time scales through the photodissociation of H_2O vapor and the subsequent escape to space of some of the resulting H_2. If so, Venus had more H_2O vapor in the past than it has at present.

Analyses of airborne observations indicate that the H_2SO_4 concentration is approximately 85 percent near the cloud tops (*8*). Using our H_2O vapor measurement at sample point 2 and applying vapor pressure arguments near the cloud bottoms, we obtain a similar concentration there. Nevertheless, the concentration of H_2O in sample 2 is approximately four times that in sample 3. Above the clouds all potential cloud-forming gases, including H_2O, have abundances on the order of parts per million. One could speculate that the almost precise mass balance implied by the low abundances of all such gases above the clouds in comparison to their abundances beneath the clouds is not the result of chance but is a reflection of evolutionary processes that lead to a rapid loss of gases, such as H_2O, when mass balance does not occur.

We next consider the implications of the GC results for the origin of the atmospheres of the terrestrial planets. Table 3 presents a summary of the inventories of volatile gases in the atmospheres of Venus, Earth, and Mars, where allowance has been made for the presence of reservoirs of some of these volatiles (for example, the H_2O oceans in the case of Earth). The columns labeled α_i show the measured mixing ratio of a given gas in the planetary atmospheres (*13*), those labeled x show an enhancement factor that takes account of the amount also present in any near-surface reservoir (it is 1 for no reservoir) (*14*), and those labeled r show the estimated ratio of the total mass of a given species to the planetary mass.

Three processes may have contributed to the volatile inventories of the terrestrial planets: (i) impacts with volatile-rich comets and asteroids (*15, 16*), (ii) capture of gaseous material from the primordial nebula of which the planets formed, and (iii) outgassing of volatiles contained in the rocks of the planetary interior. According to Table 3, the r values for Ne and nonradiogenic Ar decrease by orders of magnitude as one progresses from Venus to Earth to Mars. But estimates of the impact rate of comets and asteroids indicate that little variation is expected among the terrestrial planets, with Mars being somewhat favored in the case of asteroidal objects (*17*). The ratio of Ne to nonradiogenic Ar in the sun is about 30 (*18*), which is markedly different from the value of ~ 1/3 that characterizes both the terrestrial planets (see Table 3) and meteorites (*16*). Thus, it seems unlikely that the strong increase in r for the inert gases with decreasing distance from the sun is due to the capture of gases directly from the primordial nebula. We conclude, by elimination, that the inert gases in the atmospheres of Venus, Earth, and Mars are due to outgassing processes. The curious increase of r for the noble gases with decreasing distance apparently runs counter to the widely held view that the temperature of the primordial nebula increased markedly with decreasing distance at the time when these gases were incorporated into planet-forming material. However, alternative temperature structures are possible (*19*). Allowance for this factor, pressure trends within the nebula, as well as variations in the completeness of the degassing may lead to predictions in accord with the results in Table 3.

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Wind Velocities on Venus: Vector Determination by Radio Interferometry

Abstract. *To determine the wind directions and speeds on Venus, as each Pioneer probe fell to the surface we tracked its motion in three dimensions using a combination of Doppler and long-baseline radio interferometric methods. Preliminary results from this tracking, coupled with results from test observations of other spacecraft, enable us to estimate the uncertainties of our eventual determinations of the velocity vectors of the probes with respect to Venus. For altitudes below about 65 kilometers and with time-averaging over 100-second intervals, all three components of the velocity should have errors of the order of 0.3 meter per second or less.*

Attempts to understand the temperature and velocity distributions of Venus's atmosphere through quantitative modeling have been severely limited by the lack of three-dimensional observational constraints, especially for the altitudes below the cloud tops (*1, 2*). In order to obtain, for the first time (*3*), profiles of the vector wind velocities as functions of altitude in the atmosphere of Venus, we undertook the Pioneer Venus differential long-baseline interferometry (DLBI) experiment using the bus and the four-probe spacecraft (*4*).

In this experiment we did not measure wind velocities directly; rather, we monitored the velocity of each probe as it fell through the atmosphere. The two horizontal components of a probe's velocity, if averaged over intervals longer than a few seconds, are substantially equal to those of the ambient wind after the probe has descended to an altitude of about 65 km. Above this altitude, interpretation of the horizontal velocity measurements requires aerodynamic modeling, as does interpretation of the vertical component of the velocity at all altitudes.

For the determinations of all three velocity components, we relied upon Earth-based observations of the S-band ($\lambda = 13$ cm) radio signal that each spacecraft emitted. We combined Doppler-shift observations, which were sensitive to the projection of the velocity along the "line of sight" from the spacecraft to Earth, with long-baseline interferometric observations, which were sensitive to changes in the direction of this line. In the latter observations, an important advantage was gained by differencing the interferometric phases observed simultaneously for the bus and for each probe. The observable DLBI thus obtained is sensitive to the motion of the probe relative to the bus, but is relatively free from errors associated with the instrumentation and with the propagation medium (*4*). By the use of this differencing technique in conjunction with north-south and east-west interferometer baselines ~ 8000 km long, we are able to determine the transverse components of the probes' velocities with uncertainties quite comparable to those for the line-of-sight components.

The Pioneer Venus bus continued to follow a ballistic trajectory outside the atmosphere until after the impacts of all four probes, and its motion relative to the planet is determinable with velocity uncertainties of less than 10 cm sec^{-1} in all three components by means of conventional Doppler tracking and orbit-determination techniques (*5*). The combination of the Doppler and DLBI tracking of the bus and the probes thus can yield a determination of each probe's velocity vector with respect to Venus.

We believe that the uncertainties of our determinations, by Doppler tracking, of the line-of-sight velocities of the three small probes are each about 10 cm sec^{-1}, caused by uncertainties in the transmitted frequencies. These frequencies were controlled by onboard crystal oscillators (*6*). The large probe and the bus carried coherent transponders which enabled "two-way" Doppler observations to be made with equivalent velocity uncertainties of less than 1 cm sec^{-1}.

Redundant long-baseline interferometers were constructed for this experiment from the two antennas of 64-m diameter of the Deep Space Network (DSN) at Goldstone, California, and Canberra, Australia; and the 9-m antennas of the Spaceflight Tracking and Data Network (STDN) at Santiago, Chile, and Guam (*7*). The directional beam of each of these antennas, and the 2291- to 2293-MHz radio-frequency (RF) passband of a single receiver connected to each, included the signals from all five spacecraft simultaneously. To monitor the group and the phase delays, as well as the gains, of the receivers and all subsequent portions of our interferometry system, we also included in the RF input of each receiver a set of continuous low-level calibration signals whose frequencies spanned the passband; the signals were derived from an atomic hydrogen maser or a cesium-beam frequency standard at each site.

The entire RF band of signals 2 MHz wide was converted to the 0- to 2-MHz "video" band, then sampled at 0.24-μsec intervals, digitized with 3 bits per sample, time-tagged according to the local atomic clock, and recorded digitally on redundant magnetic tapes at each site. When the observations had been completed, the recordings were carried to the Jet Propulsion Laboratory (JPL).

There, they are filtered digitally to reduce the 2-MHz bandwidth to a set of seven spectral windows each about 1 kHz wide. Each window contains, in addition to noise, one continuous-wave signal: the carrier wave from one of the five spacecraft, or one of two band-edge calibration signals. These reduced-bandwidth data, also in digital form, are shipped to the Massachusetts Institute of Technology where the phase of each signal is estimated as a function of the time indicated by the receiving site's clock when the signal was originally recorded (*8*). Data processing, both for bandwidth reduction and for phase estimation, is proceeding as anticipated but is in-

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