best current atmospheric models indicate that r has a value of about 0.95 with a dispersion of about ± 0.03 and that r is almost independent of the model.

We have compared the theoretical calculations and the observations to obtain first-order estimates of the infrared opacity of the cloud particles and the water vapor mixing ratio beneath the clouds, α_{H_2O}. Figure 3 shows synthetic net flux profiles for the broad-band channel for three values of the infrared cloud opacity. The lower curve was computed for an infrared extinction coefficient profile, σ_{ir}, equal to the visible profile, σ_{vis}, whereas for the middle and upper curves $R = \sigma_{ir}/\sigma_{vis}$ equaled 1/4 and 1/16, respectively. Comparing these predictions with the observed values in the altitude range approximately 57 to 50 km, the location of the "middle cloud layer" (*5*), we conclude that in this cloud the observed $R \simeq 1/4$. This result seems reasonable since, in the longer wavelength region of the thermal infrared, the particle size (*5*) became small compared with the wavelength and thus we expect R to be less than 1.

For all the theoretical curves of Fig. 3, the net flux rises more slowly above 57 km, that is, in the region of the "upper cloud layer" (*5*), than does the observed profile. This difference indicates that R is significantly less than 1/4 in this cloud layer, a result consistent with the absence of large particles there. Also, the predicted decrease of the net flux within the bottom cloud layer, which spans the region from 50 to 47 km, is greater than is observed. Hence, while σ_{ir} increases from the middle to the bottom cloud layer, it does so by a smaller amount than at visible wavelengths. Analogous comparisons with the narrow-band results imply that σ_{ir} is somewhat larger in these channels than in the broad-band channel.

Figure 4 illustrates the sensitivity of the predictions to variations in the water vapor mixing ratio beneath the clouds, α_{H_2O}. Comparing these curves with the observed broad-band results below 47 km, the bottom of the main clouds, we see that a value of about 10^{-3} is required. This result is in approximate accord with other spacecraft data (*11*).

Finally, we consider the implications of the findings for the planetary heat balance. Averaged over the thermal infrared, the cloud system has an optical depth of about 7, which can be compared to a value of about 35 at visible wavelengths (*5, 9*). Thus, the clouds represent an important source of infrared opacity. We note that the amount of water vapor deduced to be present below the clouds is comparable to the amount needed to close the major CO_2 windows in the infrared and achieve the greenhouse effect (*7, 12*). Thus, the high surface temperature of Venus may be explained by the opacity of CO_2 and H_2O vapor, but with a significant assist from the cloud particles.

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Venus Lower Atmospheric Composition: Preliminary Results from Pioneer Venus

Abstract. *Initial examination of data from the neutral mass spectrometer on the Pioneer Venus sounder probe indicates that the abundances of argon-36, argon-38, and neon-20 in the Venus atmosphere are much higher than those of the corresponding gases in Earth's atmosphere, although the abundance of radiogenic argon-40 is apparently similar for both planets. The lower atmosphere of Venus includes significant concentrations of various gaseous sulfur compounds. The inlet leak to the mass spectrometer was temporarily blocked by an apparently liquid component of the Venus clouds during passage through the dense cloud layer. Analysis of gases released during the evaporation of the droplets shows the presence of water vapor to some compound or compounds of sulfur.*

The sounder probe, or large probe, of the Pioneer Venus multiprobe spacecraft (*1*) entered the atmosphere of Venus on 9 December 1978. It carried seven instruments, including a neutral mass spectrometer, designed to measure the composition of the lower atmosphere of Venus.

The mass spectrometer, a single focusing magnetic sector device (*2*), was intended to measure atomic masses ranging from hydrogen to lead. Gases were admitted to the instrument through a set of two microleaks. The leaks were hermetically sealed prior to launch by means of a ceramic cap attached to a flange in the shell of the probe behind the heat shield. The cap was broken with a pyrotechnic device, exposing the leaks to the Venus atmosphere a few seconds after the parachute was deployed and the heat shield jettisoned. Gas molecules entering the leaks passed through an ion source where they could be ionized by electrons with an impact energy of 70 eV. The electron impact energy was reduced to 30 and 22 eV on successive mass scans on three occasions during descent, providing additional aids for the identification of parent molecules, whose cracking patterns change significantly as the ambient energy is reduced from 70 to 22 eV. Additional simplification of the spectrum occurs since the production of doubly charged ions is negligible at lower impact energies.

Ambient gases were removed from the ion source by a chemical getter. The pumping speed was controlled by a valve connecting the ion source and getter. The valve was allowed to open during descent in response to increasing atmospheric pressure, maintaining in this fashion a relatively constant pressure at the ion source (*3*). Preliminary flight data indicate that the pressure in the ion source responded as expected to changes in external pressure, increasing by less than a factor of 10 while the external pressure increased by a factor of 10^3. An anomaly occurred near 50 km in a region of the atmosphere where Knollenberg and Hunten (*4*) and Ragent and Blamont (*5*) detected the presence of significant concentrations of particulate material. The conductance of the leak to the ion source decreased as though the inlet had been blocked by some foreign material. The leak remained closed for approximately 10 minutes and then gradually opened over a period of about 5 minutes, at which time the flow of atmospheric gases to the ion source was fully restored (about 30-km altitude). Operation of the spectrometer then remained normal until the signal was lost, presumably at impact.

Table 1. Abundances of ^{36}Ar and values of the concentration ratio [^{36}Ar]/[^{12}C] for the sun, Venus, Earth, and Mars.

Abundance	Sun	Venus	Earth	Mars
^{36}Ar	1×10^{-4}	$\sim 10^{-8}$	3.5×10^{-11}	1.9×10^{-13}
[^{36}Ar]/[^{12}C]	3×10^{-2}	$\sim 10^{-4}$	2×10^{-6}	1.7×10^{-5} to 6.6×10^{-8}

The operation of the mass spectrometer was controlled by a microprocessor (*6*). Two calibration gases, methane and ^{136}Xe, were introduced into the mass analyzer immediately prior to the initiation of the measurement sequence. Mass peaks associated with the calibration gases were used to provide reference points which the microprocessor could utilize to control the mass scan sweep voltage. A lookup table of nouns stored in the microprocessor defined positions in the mass spectrum of a preselected set of mass peaks. The microprocessor, scanning this table, directed the instrument to measure the amplitudes only of the preselected mass peaks. This procedure served to eliminate the time associated with the normal method of sweeping between adjacent mass numbers. Thus, the spectrum from 1 to 208 atomic mass units (amu) was scanned in 64 seconds, providing an average spatial resolution for the measurement of individual gases equivalent to approximately 1 km of altitude in the Venus atmosphere. Complete processing of data from the sounder probe should eventually provide as many as 55 mass spectra, extending from an altitude of about 68 km down to the planetary surface.

Preliminary examination of the data indicates the presence of surprisingly large concentrations of ^{36}Ar, ^{38}Ar, and ^{20}Ne. The mixing ratio (volume to volume) of ^{36}Ar in the Venus atmosphere is approximately 10^{-4}, compared to a value of 3.2×10^{-5} observed for Earth's atmosphere. The atmosphere of Venus, however, is approximately 90 times more massive than that of Earth. It follows that the absolute abundance of ^{36}Ar in the Venus atmosphere must be approximately 200 to 300 times larger than that of Earth. The abundance of ^{20}Ne is apparently also high in the atmosphere of Venus, comparable to that for ^{36}Ar. The abundance ratio [^{36}Ar]/[^{38}Ar] in the Venus atmosphere is, however, similar to values observed for Earth, meteorites, and the moon.

Table 1 gives a comparison of the abundances of ^{36}Ar reported for the sun (*7*), Venus, Earth, and Mars (*8*). Results are quoted in terms of mass mixing ratios (gram per gram), that is, ratios of the mass of atmospheric ^{36}Ar referenced with respect to the total mass of the parent body. The relative abundance of ^{36}Ar appears to decrease with increasing heliocentric distance, at least for the inner solar system. The pattern is not altered significantly if we consider the concentration ratio [^{36}Ar]/[^{12}C] (Table 1). The ratio quoted for Venus assumes that most of that planet's ^{36}Ar and ^{12}C resides in its atmosphere. The ratio quoted for Earth assumes that most of the terrestrial ^{36}Ar occurs in the atmosphere but that the bulk of the terrestrial ^{12}C is found in carbonate minerals (*9*). A range of values is given for Mars, reflecting various assumptions regarding the abundance of condensed carbon on that planet (*8*). If most of the martian ^{36}Ar and ^{12}C were to reside in its atmosphere, the ratio would be 1.7×10^{-5} g per gram.

The relative abundances of ^{12}C and ^{14}N are apparently similar on Venus and Earth (*9*), although the absolute abundance for ^{12}C (gram per gram) may be higher for Venus by about a factor of 1.5. The situation is less clear for Mars since significant quantities of ^{14}N appear to have been lost as a result of escape (*10*) and since major uncertainty is attached to present estimates for the surface-subsurface reservoirs of ^{12}C. Anders and Owen (*11*) have argued that the low abundance of ^{36}Ar and the relatively high value for the concentration ratio [^{40}Ar]/[^{36}Ar] in the martian atmosphere might be taken to indicate that Mars formed with approximately 1/35 as much carbon and nitrogen as Earth, and that Mars had degassed less efficiently than Earth (by about a factor of 4). The abundance of ^{40}Ar on Venus appears similar to that for Earth. Our data suggest that the mixing ratio of ^{40}Ar to ^{36}Ar is about 1. The presence in the Venus atmosphere of high concentrations of ^{36}Ar, ^{38}Ar, and ^{20}Ne, together with normal, by terrestrial standards, concentrations of ^{40}Ar, ^{12}C, and ^{14}N, suggests that the use of scaling procedures based on measurements of primordial noble gases to estimate abundances of other volatiles in a planetary atmosphere may be subject to error. The new data for Venus, in combination with earlier information from Mars and Earth, suggest that the concentration of primordial noble gases may vary appreciably from planet to planet, even though variations in the abundance of other more reactive volatiles such as carbon and nitrogen may be quite small.

The blockage of the inlet leaks of the mass spectrometer which occurred in a region of dense clouds may have provided an unscheduled, although fortunate, opportunity for direct measurement of at least one component of the Venus clouds. The decrease in conductance observed was quite marked. The amplitude of the primary CO_2^+ mass peak (44 amu) decreased by four orders of magnitude to a small residual background level. At the same time, the amplitudes of other peaks also declined to levels consistent with residuals to be expected if the flow were interrupted after the ion source had been exposed to a large sample of atmospheric gas. Two microleaks were used in parallel during the early phase of the descent of the probe, in order to increase gas throughput to the ion source in low-density regions of the atmosphere. The secondary leak, which had a fivefold larger conductance, was closed at 47 km by an electronically operated valve. Gases admitted to the instrument passed only through the primary leak for the balance of the descent. The blockage occurred approximately 3 minutes before the second microleak was closed, an indication that both leaks must have been blocked, presumably by material from the clouds. It seems probable that the blocking material should have been present in liquid form in order to account for the relatively complete degree to which gases were excluded during the subsequent 10 minutes.

The primary inlet leak had an external heater attached to its inlet tube to ensure that the temperature of the leak would always remain above that of the ambient atmosphere. Preflight tests in a simulated Venus atmosphere showed that the leak temperature would vary from about 20°C above ambient temperature at higher altitudes to about 5°C above ambient at lower altitudes. The heater was designed to vaporize any droplets that might lodge 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	2	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*).