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11. Although the release of latent heat could also be important in determining thermal structure (and, therefore, convective instability) within the clouds, we believe thermal radiation from below is the primary mechanism. First, the onset of the warming and in fact almost the entire thermal offset of the clouds, discussed in the text relative to Fig. 1, occurs at 40 to 50 km, that is, below the clouds, where latent heat release cannot be a factor. Furthermore, to duplicate the magnitude of the divergence in the net upward infrared flux [R. W. Boese, J. B. Pollack, P. M. Silvaggio, *Science* **203**, 797 (1979)] by latent heat release within the clouds requires that all of the droplets be transported to lower altitudes for vaporization and regenerated on a time scale of 5000 seconds. This should be accompanied by a growth in total droplet mass per unit volume with height, which is not seen in the data (*7*).
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17. This is consistent with the wind measurement at the day probe site (*15*). Furthermore, this pressure difference becomes small at the altitude (~40 km) where the measured wind velocities become small.
18. We thank O. B. Toon for helpful discussions concerning the relative importance of latent heat release and infrared radiation in the maintenance of the thermal structure in the clouds. We thank L. Pfister for many helpful discussions concerning the dynamical implications of the data.

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Composition and Structure of the Venus Atmosphere: Results from Pioneer Venus

Abstract. *Results from the Pioneer Venus sounder probe neutral mass spectrometer indicate that there is no difference in the isotopic ratios of carbon and oxygen between Venus and Earth to within ± 5 percent. The mixing ratio of nitrogen is* 3.5^{+3}_{-2} *percent with an isotopic ratio within 20 percent of that of Earth. The ratio of argon-36 to argon-40 is 85 percent, and the ratio of argon-38 to argon-36 is 20 percent. The mixing ratios of argon-36 and argon-40 are approximately 40 and 50 parts per million, respectively, with an error of about a factor of 2 (mainly toward a lesser amount) resulting from uncertainty in the response of the ion pump to rare gases. Hydrogen chloride cannot account for more than a few percent of the 36 mass peak, and therefore the large excess of primordial argon is a reasonable conclusion. The ratio of neon-20 to argon-36 of 0.5 ± 0.3 is definitely terrestrial in character rather than solar. These results indicate that there is a large excess of all primordial noble gases on Venus relative to Earth. There appears to be a considerably higher abundance of sulfur compounds below 20 kilometers than in or above the main cloud layer. The 32 and 60 mass peaks show a sharp increase below 22 kilometers, indicating the possible production of sulfur and carbon oxysulfide (COS) at the expense of sulfur dioxide.*

The mass spectrometer on the Pioneer Venus sounder probe, which entered the Venus atmosphere on 9 December 1978 (*1*), measured the atmospheric composition relative to CO_2, the dominant constituent, from an altitude of 61 km to the surface. The instrument, a single-focusing, magnetic-sector spectrometer (*2*), scanned the mass range from hydrogen through mercury with a dynamic range of six decades. Because the instrument was designed to measure atmospheric composition rather than density, a gate valve (*3*), operated by the increasing atmospheric pressure encountered during descent, was installed to control the ion source pressure to a relatively constant value as the inlet leak throughput continually increased. The result was as follows: (i) a sensitivity of 1 part per million (ppm) was attained throughout most of the descent while the atmospheric pressure changed by four orders of magnitude and (ii) the instrument output signals are not related directly to atmospheric density but are relative to CO_2. Figure 1 is the altitude profile of CO_2 in terms of instrument output signal (related to counting rate). Since this is not a density profile but a measure of the partial pressure of CO_2 in the ion source, all other data will be presented as mixing ratios relative to this CO_2 profile.

The decrease in signal starting at 51 km is caused by a blockage of the inlet leak, which occurred after the probe passed through most of the cloud layer designated region C of the nephelometer data (*4*). This blockage occurred presumably as a result of an overcoating of cloud materials (hydrated H_2SO_4 droplets) which lasted until the probe emerged from the lower haze layer at 31 km (*5*), at which time the flow of atmospheric gases resumed.

The isotopic ratios of C and O, ^{13}C to ^{12}C, and ^{18}O to ^{16}O have been found to be close to Earth values. The C ratio from the CO_2^{2+} peaks at mass 22 and 22.5 is about 0.012, approximately 5 percent higher on Venus than on Earth, with a standard deviation of ± 5 percent. The 45/44 mass peak ratio (CO_2^+) yields, on the average, a similar number. The $^{18}O/^{16}O$ ratio was within 1 percent of the Earth value (0.00204), also with a standard deviation of ± 5 percent.

In order to determine the N_2 abundance on Venus from the mass spectrometer data, several methods were used. Because of the rather large production of CO from CO_2 in the ion source, the 28 mass peak is comprised of both CO^+ and N_2^+ (the majority being CO^+). The CO^+ peak amplitude is a function of the degree to which the gate valve to the ion source pump (a chemical getter pump) was open, and its ratio to CO_2^+ varied from 0.4 when the valve was closed to 0.12 when the valve was wide open. On the basis of data from the lowest part of the descent profile and corrections for the CO contribution, the N_2 mixing ratio was found to be approximately 2.5 percent. However, the uncertainty in the result is fairly large, at least 50 percent.

A second method is to derive the N_2 content from the 29/28 mass peak ratio. If the nitrogen isotopic ratio is equivalent to that in Earth's atmosphere and if the 29 mass peak consists entirely of the ^{13}C and ^{15}N isotopic peaks (which does not appear to be true between 20 and 5 km), the N_2 mixing ratio was found to be 3 percent below 5 km and approximately 4 percent above the dense cloud layer. The uncertainty is of the order of 50 percent. Because of the magnitude of the uncertainties, there is no implication in these numbers that the atmosphere is anything but well mixed. If the nitrogen isotopic ratio were increased by 20 percent, the N_2 mixing ratio would increase by 1.5 percent. For a 70 percent increase in the $^{15}N/^{14}N$ ratio, as was found on Mars (*6*), the 29/28 mass ratios for both C and N would become equal and it would be impossible to determine the N_2 abundance by this method. However, since the 29/28 mass peak ratio is 0.103, the maximum allowed enhancement in the $^{15}N/^{14}N$ ratio would be 35 percent. This value would require the entire 28 mass peak to be N_2, which it clearly cannot be. It therefore appears that the most probable value of the nitrogen isotopic ratio is close to that on Earth.

The third method for determining the N_2 abundance is based on the peak at 14 atomic mass units (amu), which consists of a mixture of ^{14}N, CH_2 from methane, and CO^{2+} and N_2^{2+}. If corrections are made for methane and doubly charged

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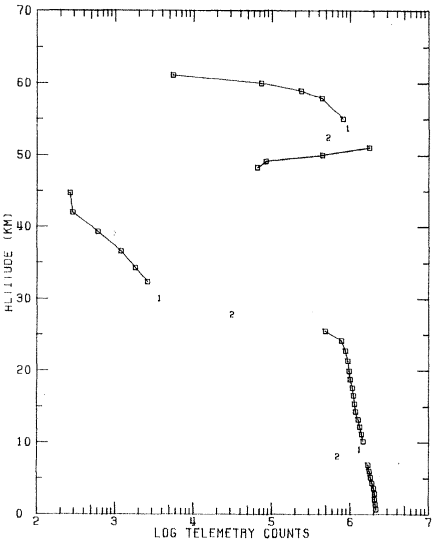

Fig. 1. The CO_2 counting rate as a function of altitude; *1* and *2* indicate times when the ion source electron energy, normally 70 eV, was reduced to 30 or 22 eV, respectively.

ions, the N_2 mixing ratio from the 14 mass peak is 4 percent above the clouds and 6 percent near the surface. At the low altitude the methane correction becomes very large, which increases the uncertainty in the measurement.

From all of these data, the best estimate of the N_2 mixing ratio in the Venus atmosphere is 3.5^{+3}_{-2} percent. This value compares favorably with the values from the gas chromatograph on the sounder probe (*7*) of 4.6, 3.5, and 3.4 percent at 54, 44, and 24 km, respectively, and with
The value for the Venera 9 and 10 mass spectrometers was 1.8 percent (*9*).
extrapolated to the lower atmosphere. The value for the Venera 9 and Venera 10 mass spectrometers was 1.8 per-

One of the discoveries from the mass spectrometer data reported earlier (*1*) is the surprisingly large concentration on Venus of primordial ^{36}Ar and ^{38}Ar, in a ratio of 5 to 1, which seems to be a constant among the bodies in the inner part of the solar system. The isotopic ratio of ^{36}Ar to ^{40}Ar is 0.85, with an error of ±10 percent. The mixing ratio of ^{36}Ar is 40 ppm with an error of a factor of 2, mainly toward a lower value. This yields a ^{40}Ar mixing ratio of approximately 50 ppm with a similar uncertainty. The error in the measurement stems from the use of a sputter-ion pump as the sink for rare gases that enter through the inlet leak. The ion pump is attached to the mass analyzer section of the instrument, separated from the ion source by the very small object slit. The ion source pump is a chemical getter which does not pump rare gases. Because the pumping speed of an ion pump for rare gases is somewhat lower than for CO_2 and since such pumps tend to regurgitate rare gases when pumping a heavy load of active gases (such as CO_2), there is some uncertainty about the absolute concentration of rare gases in the instrument. The measured values thus tend to be upper limits. Moreover, these values increase with time throughout the descent, as seen in Fig. 2.

Therefore, we found that the best course was to determine the mixing ratio of ^{36}Ar near the beginning of the descent, above 50 km, before the pump had time to accumulate much Ar. The decrease in ^{36}Ar counts relative to the 44 mass peak counts as seen in the top four points (Fig. 2) is caused by a slower rise in the 44 peak amplitude than in the 36 peak, presumably due to pumping by the walls of the ion source cavity. When equilibrium was reached, the ratio measurement was obtained. Appropriate correction factors for ionization efficiency have been applied. The 40 mass peak had a preentry background amplitude which increased during entry as a result of the vibration of the pump (a well-known phenomenon); thus it was not possible to obtain an absolute determination of the ^{40}Ar mixing ratio. Therefore, the isotopic ratio of Ar was determined from the portion of the flight below 25 km, after the pump had been exposed to a considerable quantity of Venus atmospheric Ar. Of course, suitable corrections were made for background peak amplitudes. The ^{40}Ar mixing ratio was then determined from that for ^{36}Ar and the Ar isotopic ratio. The $^{36}Ar/^{38}Ar$ mixing ratio was the same above 50 km as below 25 km; this result demonstrates the validity of using the low-altitude portion of the descent for isotopic ratio measurements.

The gas chromatograph has measured an increasing Ar mixing ratio with altitude (from 18 to 30 ppm), but the higher value has an uncertainty that includes the lower value (*7*). The reverse is not true. It seems, at this time, however, that the Ar concentrations determined by the mass spectrometer are somewhat larger than the gas chromatograph values (18 ppm at 24 km), even if allowance is made for the problems caused by the ion pump. The Venera 11 and Venera 12 mass spectrometers measured a value of 150 ppm for all isotopes with the radiogenic content (^{40}Ar) equal to the sum of the ^{36}Ar and ^{38}Ar, which agrees closely with the present value (*10*). However, the Venera 11 and Venera 12 gas chromatograph value was 40 ± 20 ppm (*11*). Thus it appears that the mass spectrometer results from both Venera and Pioneer Venus tend to be higher than the gas chromatograph data. These results suggest that perhaps the ion pump enhancements are not properly accounted for or that there is some systematic error in the gas chromatograph data.

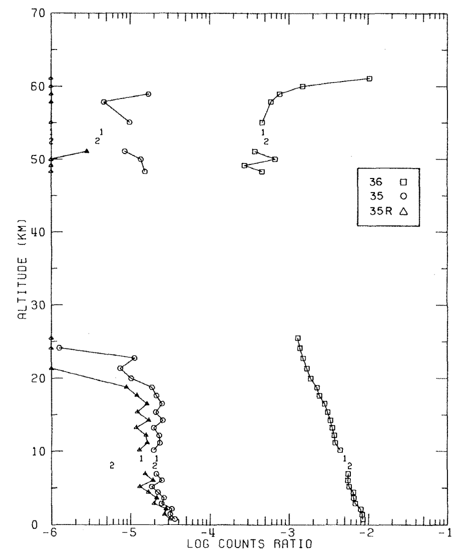

Fig. 2. Counting rate for the 36 and 35 mass peaks relative to the counting rate for the 44 mass peak as a function of altitude. The curve labeled "35R" is the 35 mass peak less a background counting rate.

The question of whether the 36 mass peak might not be due to HCl instead of ^{36}Ar can be answered on the basis of a consideration of the mixing ratio of the 35 mass peak (Fig. 2), which is seen to increase with decreasing altitude but less steeply than Ar. There is a background of scattered ions in the mass spectrometer on the low mass side of a very large ion peak (in this case CO_2^+), which increases with increasing pressure in the mass spectrometer. This amounts to the order of 10 to 15 counts at the 35 mass peak position.

The cracking pattern for HCl as determined by the flight spare instrument based on the use of 70-eV electrons yields a 36/35 mass peak ratio of 7.0. Therefore, if the 35R mass peak (background subtracted) is entirely Cl from HCl, the HCl contribution to the peak at 36 amu is everywhere less than 2 percent. Even without subtracting the background and assuming that the entire 35 mass peak is due to Cl (which it most probably is not), one finds that the HCl contribution to the 36 mass peak is less than 8 percent at the beginning of the descent and drops to less than 3 percent at the end of the flight. The isotopic ratio of Cl on Earth ($^{37}Cl/^{35}Cl$) is 0.326. On Venus the 37/35 mass peak ratio varies from 0.5 to 3, an indication that some substance besides Cl is a major contributor to at least the 37 mass peak. The fact that the primordial Ar isotopic ratio (found to be independent of altitude) is very close to that observed for Earth, Mars, the moon, and meteorites also argues against any appreciable HCl contribution to the 36 and 38 mass peaks. From these arguments we conclude that the large excess of primordial Ar is a valid result and that the mixing ratio of HCl in the lower atmosphere of Venus is less than a few parts per million.

The principal Ne isotopes at 20 and 22 amu are primordial. It is unlikely that the isotope at 22 amu will yield a value of the Ne mixing ratio because of the large CO_2^{2+} peak of 20,000 to 60,000 counts. Even at an electron energy of 30 eV, the CO_2^{2+} account for the entire 22 mass peak. When 22-eV electrons are used, essentially no Ne is ionized. A value of the Ne content of the Venus atmosphere was determined from the ratio of the 20 mass peak, after correction for $^{40}Ar^{2+}$ and the difference in ionization efficiencies of Ne and Ar, to the ^{36}Ar mass peak. This ratio is 0.5 ± 0.3. This result was also taken from the lower part of the flight data because of the rare gas peak enhancement right after entry, referred to above. Here also the uncertainty is quite large because of the unknown action of the ion pump on rare gases. It is clear, however, that the $^{20}Ne/^{36}Ar$ ratio is less than unity and is nearly the Earth value of 0.57. This result would tend to preclude a large accumulation of primordial gases from the sun since the solar wind $^{20}Ne/^{36}Ar$ ratio is of the order of 50 (*12*). An additional argument against the sun as a source for the excess primordial gases on Venus is that the present-day solar wind flux fails to account for the abundance by some seven orders of magnitude. Of course, there might have been a considerably larger flux sometime in the past, but it would have had a very different Ne/Ar ratio than at present.

The $^{20}Ne/^{36}Ar$ ratio of 0.5 compares favorably with that ratio obtained by the gas chromatograph (*7*), based on the assumption that ^{36}Ar is approximately 45 percent of the total Ar measured by the gas chromatograph. Thus, whatever is causing the discrepancy in mixing ratio determined by each instrument appears to be affecting both Ne and Ar in a similar manner. The Venera 11 and Venera 12 mass spectrometers obtained a value for ^{20}Ne of 10 ppm (*10*), which is at the lower end of the present range of values but within the error range.

In order to determine the Kr abundance in the Venus atmosphere, we compared the total number of counts of the 84 mass peak in the first 12 spectra (to the point of leak blockage) to the total of the 44 mass peak counts. There were only four counts at mass 84, which gives a mixing ratio of less than 1 ppm for ^{84}Kr. It is not clear whether any of the 84 mass peak counts are spurious, although the ^{83}Kr and ^{82}Kr mass peaks have no counts in any of the first 12 spectra. Therefore, an upper limit of 1 ppm for Kr appears reasonable. The Venera 11 and Venera 12 mass spectrometers obtained a value of 0.5 ppm for the ^{84}Kr mixing ratio (*10*). These numbers do not rule out a large excess of Kr on Venus, which would be consistent with the excess of the other primordial gases.

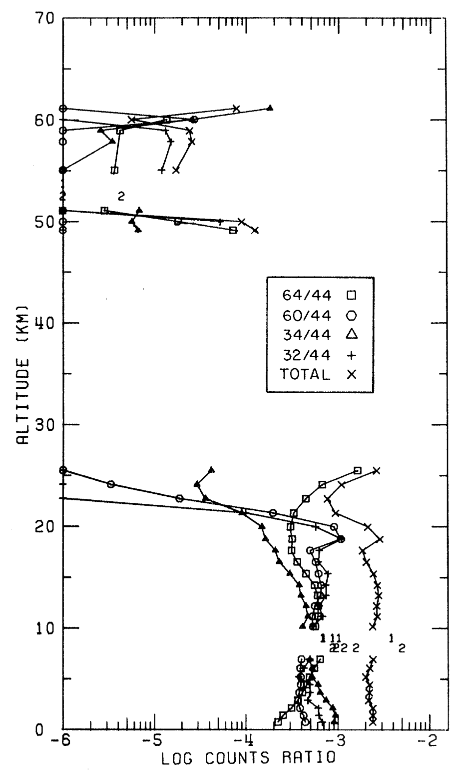

Fig. 3. Counting rates of several S compounds (identified by mass number) relative to the counting rate for the 44 mass peak as a function of altitude. The curve labeled "TOTAL" is the sum of the counting rates for the four curves shown plus the counting rates for the 48 and 96 mass peaks.

It was not possible to determine the ^{4}He content of the Venus atmosphere because of the very high residual He peak (20,000 counts) which resulted from backfilling the sounder probe with a mixture of 1 percent He in N_2 before launch. A slow leakage through glass feedthrough insulators and other possible microscopic leaks (10^{-12} cm^3/sec at standard temperature and pressure or less) during the 5 months the He was in the probe before encounter produced the accumulation.

There is considerable evidence for the existence of S compounds in the lower atmosphere of Venus (Fig. 3). The several curves are ratios of counting rates relative to the 44 mass peak (Fig. 1). The curve labeled "64/44" is most likely due to SO_2 with possibly some addition of S_2 in the lower portion. The 64/44 curve turns up above 25 km because there appears to have been a source of SO_2 in the droplet that blocked the leak. The curve labeled 60/44 has had 1 percent of the 78 mass peak (an artifact) subtracted from it. The residual (plotted) is most likely COS. The 34/44 curve has been corrected for ^{18}O and ^{34}S by subtraction of 0.4 percent of the $^{16}O_2$ and 4.4 percent of the ^{32}S measurements. This mass peak is at the H_2S mass defect position but is not well resolved from the ^{34}S mass peak position. It is assumed, at present, that this peak is from H_2S. The 32/44 mass peak is either O_2 or S; 10 percent of the 64 mass peak and 0.01 percent of the 44 mass peak have been subtracted from it. The position of the peak in the spectrum favors the S mass defect, although the mass difference is only 1 part in 1800. The curve labeled "TOTAL" is a sum of the 64/44, 60/44, 34/44, and 32/44 curves plus the 48 and 96 mass peak counts. The 48 mass peak profile closely follows that of the 64 mass peak, and the 96 mass peak does not exceed 13 counts with an average of seven counts.

The most interesting feature of these data is the sudden appearence of the 32 and 60 mass peaks below 22 km. It appears as though there might be a substantial production of S and COS, possibly at the expense of SO_2. Moreover, there seems to be considerably more S below the main cloud layer (~ 50 km) than in or above it. The dip in total S centered at 22 km is not presently accounted for but could result from a mismatch in ionization efficiencies between the various S compounds or a slow pumpout of SO_2 from the large excess acquired from the droplet on the leak.

Unfortunately, the gas chromatograph's lowest sample was taken at 24 km, at the point where the 60 mass peak reached its minimum value. The negative result reported from that instrument (*7*) is consistent with the present data.

A warning needs to be heeded at this point in the data analysis. Although the mass peaks measured in the spectrum are real, it is not clear that all of the chemical reactions (for example, COS production) are occurring in the atmosphere. Until further laboratory work has been completed, it is uncertain how the inlet system, which is at atmospheric temperature, is affecting the results.

In addition, there are significant peaks in the mass spectrum indicating the presence in the ion source of H_2O vapor (more than one would expect to be of atmospheric origin), mass 75 (an artifact peak), and methane (higher than the calibration gas amount). The effects of these substances on possible chemical reactions occurring in the ion source remain to be evaluated. In addition to these laboratory studies, we are also investigating the mass defect information contained in the descent data in the hope that we might be able to better identify the atmospheric constituents.

J. H. HOFFMAN
R. R. HODGES, JR.
Center for Space Sciences,
University of Texas at Dallas,
Richardson 75080
M. B. MCELROY
Center for Earth and Planetary
Physics, Harvard University,
Cambridge, Massachusetts 02138
T. M. DONAHUE
Department of Atmospheric and
Oceanic Sciences, University
of Michigan, Ann Arbor 48105
M. KOLPIN
Physics International,
San Leandro, California 94577

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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 (PVGC) (*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 O_2 and SO_2 prior to entry, reduce the sensitivity for Ar? (ii) Was the O_2 peak misidentified as ^{36}Ar because the column actually separated ^{36}Ar from ^{40}Ar?

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 regeneration procedure. The regeneration sequence admitted a gas mixture of O_2 and SO_2 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 H_2, O_2, Ne, CO, N_2, 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, N_2, O_2, 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 ^{36}Ar/^{40}Ar separations did not occur. We did not run these tests prior to flight since we did not have available an enriched source of ^{36}Ar. However, the differences in the mass spectrometric data (*2*) by comparison with the gas chromatographic data suggested that perhaps the misidentification of O_2 for ^{36}Ar 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 ^{36}Ar, ^{38}Ar, and ^{40}Ar (*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 N_2 and CO (Fig. 1), demonstrating the inseparability of the three Ar isotopes. The O_2 peak retention time is between the N_2 and the Ar peak. In addition, the chromatogram demonstrates that O_2 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 O_2 could have been derived from the thermal or catalytic breakdown of SO_3 in the inlet system. Concern for this possibility arises from the fact that 1 mole of SO_3 could thermally degrade to 1 mole of SO_2 and 1/2 mole of O_2 (*5*); our data show a ratio of exactly 2.68/1 for SO_2/O_2 for both the second and third samples in which both components were measurable.

When SO_3 was passed through a simulated inlet system at different temperatures, no significant release of O_2 and SO_2 occurred (Table 3). Thus any SO_3 component and ostensibly H_2SO_4 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