

2 mint

GCA-TR-73-3-N

132766

MASS SPECTROMETRIC DETERMINATION OF THE COMPOSITION OF THE VENUS CLOUDS

R. F. K. Herzog

(NASA-CR-132766) MASS SPECTROMETRIC
DETERMINATION OF THE COMPOSITION OF THE
VENUS CLOUDS Final Report (GCA Corp.)
25 p HC \$3.25
24

N73-25876

G3/30
Unclas
06813



Bedford, Massachusetts

FINAL REPORT
Contract No. NAS5-23099

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

April 1973

GCA-TR-73-3-N

MASS SPECTROMETRIC DETERMINATION OF THE COMPOSITION
OF THE VENUS CLOUDS

R. F. K. Herzog

GCA CORPORATION
GCA TECHNOLOGY DIVISION
Bedford, Massachusetts

FINAL REPORT

Contract No. NAS5-23099

April 1973

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

TABLE OF CONTENTS

<u>Section</u>	<u>Title</u>	<u>Page</u>
I	INTRODUCTION	1
II	GENERAL CONSIDERATIONS IN REGARD TO INSTRUMENTATIONS TO DETERMINE THE COMPOSITION OF THE CLOUDS ON VENUS	4
III	DIRECT ANALYSIS OF THE GAS PHASE ATMOSPHERE	5
IV	THE MASS ANALYZER	7
	A. Magnetic Analyzer	7
	B. Quadrupole Analyzer	7
	C. Monopole Analyzer	7
	D. Time of Flight Mass Spectrometer	8
V	PRE-SEPARATION OF THE CLOUD PARTICLES FROM THE AMBIENT ATMOSPHERE	9
	A. Condensation on a Cold Surface	9
	B. The Cyclone Type Separator	9
	C. Electrostatic Separator	9
VI	DETECTION OF FERROUS CHLORIDE WITH A MASS SPECTROMETER	10
VII	RECOMMENDATIONS	19
	REFERENCES	21

SECTION I

INTRODUCTION

During the last few years our knowledge of the atmosphere of Venus has been greatly improved by the Russian Venera Landing Probes and by the American Mariner Fly-by Probes. Since the results of these investigations are of prime importance for future instrumentation, they will be summarized here briefly. The literature about the subject is quite large and only a fraction of the more important and more recent papers are included here. Earlier results which are superseded by later measurements will not be included in this report.

The most important results have been obtained from the Venera probes, especially from Venera 7 which succeeded in soft landing on the surface of planet Venus. The preliminary results of these measurements have been reported by Avduevsky, et al. (Ref. 1) and the final evaluation by Marov, et al. (Ref. 2). The probe was parachuted to the surface and measured temperature and pressure from about 55 km height down to the surface. The velocity of the probe was measured by the Doppler frequency shift, and was about 100 m/sec at 50 km, and 40 m/sec at 38 km, and 20 ± 10 m/sec below this altitude. In this altitude range, there were several unexplained sudden changes of the velocity. The altitude at any moment can be calculated from the velocities. The main objective of this probe was to perform a soft landing. Since time is rather limited during which such a probe can withstand the extreme heat near the surface a relatively fast descent was purposely chosen and permitted the probe to operate for 20 minutes after the landing.

It was found that the temperature rises almost linear from 300°K at 55 km to $747 \pm 20^{\circ}\text{K}$ at the surface. The pressure rises nearly adiabatic from 10 kg cm^{-2} at 28 km to $90 \pm 15 \text{ kg cm}^{-2}$ at the surface. The adiabatic structure justifies the assumption of convective mixing and little absorption of solar radiation below 50 km.

In addition, Venera 7 has performed a rough analysis of the composition of the atmosphere of Venus. The instrumentation and the results are described in a paper by Vinogradov, et al. (Ref. 3) The results have been obtained by specific absorptions which result in measurable pressure reductions. The result is that the atmosphere consists almost entirely of carbon dioxide, Nitrogen and the rare gases together contribute less than 2 percent, Oxygen less than 0.1 percent. The water content is relatively small, between 6 and 11 mg/l , in the pressure range between 2 and 0.6 kg cm^{-2} above and below this range the water content decreases rapidly.

Kolosov, et al (Ref. 4) studied the fluctuations, of the radiowaves from the parachuted probes and found an inversion of the refraction coefficient which he associates with the lower edge of the cloud stratum at an altitude of 47 km.

The results of the American Mariner V Fly-by data have been summarized by Rea. (Ref. 5) They are based on the S-band occultation if the radiowaves have to pass the atmosphere of Venus. He concludes that there exists an optically thin cloud layer with a top altitude of 81 km where the temperature and pressures are 175°K and 3 mb respectively. He concludes further from reflection and emission spectra and from polarization data that these clouds consists probably of droplets of HCL-H₂O. There is an optically dense cloud of unknown composition at the lower level at an altitude of 61 km where temperature and pressures are 260°K and 240 mb respectively.

Further analysis of the Mariner IV to VII Fly-by experiments has been made by Rasool (Ref. 6) He found that the diurnal temperature variations are small (less than 5°K) which implies that there are strong zonal circulations up to an altitude of 70 km and a pressure of 100 mb or less. This would require horizontal wind velocities of 100 m/sec which does agree with the observation of the movement of ultraviolet features in the clouds of Venus as observed from Earth's observatories. Gold and Soter (Ref. 7) have observed that these features circle around Venus once every 4.0 ± 0.5 days. Rasool and Stewart found also that there exist two lower cloud layers where the temperatures are 350 and 450°K. These temperatures exclude water as a constituent of the clouds.

Ground observations of the spectrum of Venus were performed by Irvine, et al (Ref. 8) and interpreted by Kuiper (Ref. 9) who assumes that the cloud consists of partially hydrated ferrous chloride. This interpretation has been challenged by Chuikshenk and Thorson (Ref. 10) who states that the observed absorption bands mia 0.5 μ m and 0.39 μ m are not characteristic enough to permit positive correlation to a specific material. Plummer (Ref. 11) also disagrees with Kuiper's interpretation and states that the results could be explained by clouds consisting of ice. On the other hand, Schorn and Young (Ref. 12) disagree with Plummer and state that the experimental results show no convincing evidence of ice particles. O'Leary (Ref. 13) studied the halo of Venus and found from photometric observations that measurements evidence for ice in the Venus clouds. This conclusion has been challenged by Lewis (Ref. 14) and supported by Fukuta, et al. (Ref. 15)

Donahoe (Ref. 16) lounges the hypothesis that polywater might be present on Venus. Polywater can exists at much higher temperatures as regular water and he thinks that special conditions during the formation of this planet might have enriched this compound. Recently, the basic existance of polywater, even on Earth, has been under severe attack and the whole matter is still unresolved.

From all these controversial papers, it can be concluded that the planet Venus has probably several cloud layers of different compositions. The possibility for ice in the upper cloud layers is not excluded but highly improbable. Due to the very high surface temperature and also the high temperature at the lower cloud layers, one must except the possibility to find there materials which are not feasible in the Earth's atmosphere.

The most extensive theoretical study of the possibilities for different cloud materials has been performed by Lewis (Ref. 17). He first challenges the experimental results about the water content obtained from the Venera probes. These data were obtained by measuring the conductivity of phosphor-pentoxide, under the assumption that the atmosphere contains pure water vapor. If simultaneously HCl is present, this would increase the conductivity tremendously and a much smaller water content would be adequate to explain the observed increase in conductivity. Thus a much lower water content, as the one obtained from the Venera probes is probable and is confirmed by spectroscopic data. This small water content is not sufficient to obtain a dense cloud layer. Nevertheless the outer most haze may consist of highly concentrated H₂O-HCl droplets, possibly with a small fraction of ice particles. Lewis assumes that all cloud layers consists of mercury or mercury compounds. He first calculates that the total amount of mercury which is contained in the crust of planet Earth is quite sufficient to provide the mercury necessary for the formation of the Venus cloud layers. Due to the higher surface temperature on Venus, it is impossible that either mercury metal or any of its compounds can be retained on the surface. He studies all possible compounds between the volatile elements H, C, N, O, S, Cl, F, Hg, I, and Br. His conclusion is that the principal cloud species are most probably Hg₂Br₂, Hg₂I₂, HgS, Hg, and Hg₂Cl₂. The visible cloud deck on Venus at a temperature near 240°K is compounded of a thin haze of Hg₂Cl₂ overlying a dense cloud of liquid Hg droplets. The possibility of additional compounds of other volatile elements contributing to the formation of the clouds is not discounted. He further states: "It appears that Earth-based astronomical techniques have nearly reached the end of the road insofar as their capabilities to provide new data about atmospheric structure and composition are concerned. Any substantial improvement in our current knowledge of the atmosphere and clouds of Venus must rely upon the use of carefully designed atmospheric entry probes".

Oboukhov and Golitsyn (Ref.18) have studied intensively all the available experimental data. The present situation is best summarized by his statement: "The most difficult problem for Venus is now without a doubt, the nature and composition of the clouds. From the measurements of water vapor content made by the Venera stations it would seem that the clouds should be of liquid water at the lower levels and of ice particles in the upper part. However, spectroscopic determinations of the H₂O content give concentrations 2 or even 4 orders of magnitude less. Polarization measurements suggest spherical particles of the order of 1 μm in diameter with a refractive index n= 1.45 to 1.50 which excludes water or ice. There are purely chemical difficulties with the water. If there were much water, then we could not observe HCL the quantities existing there. Other proposed compounds like FeCl₂ · 2H₂O or mercurous halides also introduce various chemical observational difficulties. One should not exclude the possibility that there are several cloud layers on Venus of various natures. The problem could be resolved by direct mass spectrometric or other measurements within the atmosphere of the planet during the descent of an automatic station."

SECTION II

GENERAL CONSIDERATIONS IN REGARD TO INSTRUMENTATIONS TO DETERMINE THE COMPOSITION OF THE CLOUDS ON VENUS

The most serious difficulty for such an instrument is the required extremely high sensitivity. Lewis (Ref. 17) presents some figures in Table V of the probable composition at the 240°K level. In this model, the atmosphere consists of 95 percent CO₂ and 5 percent N₂, and only trace amounts of other materials. The most important ones are H₂O about 100 parts/million, HCl 1 part/million, Hg 0.05 parts/million, HgI₂ 0.05 parts/billion. The concentrations of the other mercuric halides are even less. It can be assumed that the concentration of mercury may be higher at other altitudes, but even then it will probably stay below the detection limits of normal mass spectrometers.

This problem can be attacked in the following two ways: (a) collection of the cloud particles and separation from the CO₂ atmosphere before the introduction into the mass spectrometer, (b) increased sensitivity of the mass spectrometer for these impurities.

An additional difficulty comes from the fact that the time which is available for performance of the analysis is too short. Every attempt has to be made to increase the time spent in the cloud region. A larger parachute and opening of the parachute at higher altitudes will achieve this goal to some degree. Since it is expected that the different cloud layers have different composition, it would be desirable to have an instrument which responds rapidly to a change in the composition. Unfortunately this requirement is contradictory to the necessary high sensitivity. Therefore, a compromise is necessary by integrating the composition over several altitude ranges.

SECTION III

DIRECT ANALYSIS OF THE GAS PHASE ATMOSPHERE

If such a measurement is performed with sufficient sensitivity, then it can be assumed that the cloud material will be detected in the atmosphere below. This will be true if we exclude the possibility of dust clouds which have been observed on planet Mars. The inlet system and ion source has to be heated sufficiently to prevent condensation of the cloud droplets in the inlet system. The evaporation of those droplets in the inlet system will enrich the gas samples with the materials which are of special interest. In order to achieve a fast response of the instrument, it will be necessary that the ambient atmosphere flows directly by the capillary leak in the mass spectrometer inlet system. Any tubulation in front of the leak would restrict this flow. If such a tubulation should be necessary, it should have two openings one entrance opening on the lower end of the parachuted instrument and another one of the upper end in order that a large amount of gas can flow through this tube. The capillary leak would be in the side wall of this tube or protruding inside.

In order to obtain the required high sensitivity, it will be mandatory that optimum pressure is always achieved in the ion source. For a conventional Nier type ion source, this is approximately 1×10^{-4} torr. Since the ambient pressure of the atmosphere in the different cloud layers increases several orders of magnitude, it will be necessary to adjust the leak rate accordingly. Variable leaks with automatic pressure regulators for laboratory use have been developed by the Granville-Phillips Corporation. However, it is doubtful that such a leak can be sufficiently miniaturized for a space probe. In addition, the motor driven device may not have the required reliability. If the cloud contains solid matter which cannot be evaporated, it may block the leak and all measurements at lower altitudes would be lost. The same is true for a second approach, which would utilize only one small leak and operate the pumps for the evacuation of the ion source, with low pumping speed at higher altitudes and with high pumping speed at lower altitudes. This change in the pumping speed can be easily performed by raising the temperature of a getter pump. A third approach to the leak problem is to utilize several leaks of different sizes for different altitudes. The main advantage of this approach is that if one leak should be blocked by dust only a part of the measurements would be lost until the next leak is opened. The technical difficulties of this approach are also considerable. Because the first leaks for the higher altitudes are larger than the later ones, each leak has to be closed tight before the next one can be opened for the measurements at the lower altitudes.

The fourth approach is to utilize the hydrogen type gas chromatograph which has been developed for Mars by Lovelock, et al. (Ref. 19). For the application to analyze the clouds of Venus, it would not be necessary to use the gas chromatograph feature of this device. In this case, the hydrogen column would act mainly as a restriction of the gas flow which can be easily regulated by changing the voltage on the electrolytic cell. The capillary through which this hydrogen sample mixture flows is relatively wide and therefore blocking of this capillary by cloud dust is unlikely. Since this device has already been developed for a space application, only little additional work would be necessary to adapt it for the application on Venus. The main disadvantage is the time delay between the introduction of the sample and the arrival of the sample at the mass spectrometer ion source. This time delay is of no consequence for the application on Mars where there is plenty of time available to perform the analysis. However for the application on Venus, the time during the descent of the parachuted instrument is quite limited. Therefore it would be necessary to reduce this time delay to less than 1 minute, which probably can be done by appropriate choice of the capillary dimensions and gas flow. Even if this can be achieved it will be rather difficult to correlate the obtained spectra with the correct altitude at which the sample has been taken. It can be seen from the above, that the inlet system is one of the main obstacles for the development of this instrumentation.

Another important part of the mass spectrometer system are the pumps which are necessary to maintain a sufficiently low pressure in the analyzer. The main pumping action can be performed by getter pumps. It will require a special study to determine which getter material is best suited for a gas load which consists mainly of CO_2 . Unfortunately no getter material is available which will pump rare gases. Since the existence of rare gases in the atmosphere of Venus can not be completely excluded, an additional pump with relatively low pumping speed is necessary to remove all rare gases. This pump can be either an ion pump of the appendix type or an "Orb Ion" pump. The choice depends on the type of mass analyzer. If a magnetic mass analyzer is used, then the magnetic field of a regular ion pump does not do any harm. This pump has the advantage that it is fully developed and readily available. If a quadrupole or monopole mass filter is used, it has to be well shielded against the magnetic fringe field of the ion pump. In this case, an Orb Ion pump is preferable because it does not need any magnetic field and will result in a considerable weight reduction of the whole system. The performance of the Orb Ion pumps have been tested extensively by Herzog (Ref. 10) who found that a good pumping speed even for argon can be obtained with a very small power consumption. Some development work would be necessary to make this pump rugged enough for space application.

SECTION IV

THE MASS ANALYZER

Here we have the choice between four different analyzers: (a) a magnetic analyzer, (b) a quadrupole analyzer, (c) a monopole analyzer, and (d) a time of flight mass spectrometer. Each one has its peculiar advantages and disadvantages which will be discussed briefly.

A. Magnetic Analyzer

The main advantage of this instrument is that it has been fully developed and flight tested. In order to obtain the wide mass range necessary to cover the mercury halides, it would be necessary to work with a reduced acceleration voltage. Under these conditions, it is doubtful that a trace sensitivity of better than 1 part/ million can be achieved. One alternative to avoid this difficulty is to operate the ion source with an electron energy of several hundred volts. This will result in complete fragmentation of the heavy molecules and will also produce doubly charged mercury ions at relatively large intensity. In this case, a mass range up to Mass 127 (for iodine) would be sufficient because the doubly charged mercury ions will appear in the mass range 98 to 102. This approach will also be useful if a quadrupole or monopole analyzer is used. However, accurate determination of the specific mercury compound will be more difficult.

B. Quadrupole Analyzer

These analyzers have also the advantage that they are fully developed and flight tested. However, the high mass range requires a rather high RF voltage and consequently a large power consumption.

C. Monopole Analyzer

A detailed comparison of the monopole with the quadrupole analyzer has been performed by Herzog (Ref. 20). It has been shown that the power consumption of the monopole is about 1/4 than that of a quadrupole of the same basic dimensions. This is a distinct advantage for an instrument for a space application where the available power is quite limited. It has been found with the laboratory model that the dynamic range of the monopole instrument is approximately 1 part/million. This range is mainly limited by scattered ions which produce a general background. It can be expected that a tandem monopole instrument would reduce this background and provide an increased dynamic range. Both monopoles of the tandem arrangement can be operated from the same power supply. The fine adjustment of the second analyzer in relation to the first one can be performed by adjusting the dc to ac voltage ratio. This approach to achieve a very wide dynamic range should be pursued further.

D. Time of Flight Mass Spectrometer

The time of flight mass spectrometer has several advantages. The required large mass range does not cause any difficulty nor does it require a higher power consumption or an increased weight of the instrument. It only means that the repetition frequency of the ion pulses has to be sufficiently reduced to avoid an overlap of the spectra. The second advantage is that all masses are measured simultaneously. Therefore this instrument could provide, in principle, a better height resolution than all the other instruments which are using a scanning method which requires several seconds to cover the whole mass range. Unfortunately, only the main constituents of the sample can be measured with each pulse. The intensity of the minor constituents is so small that integrations over several pulses are necessary to obtain a usable signal. Although some time of flight mass spectrometers have been flown, they are not developed to such a degree as the instruments A and B. The far more complicated electronics has an unfavorable effect on the reliability. A combination between the laser beam ion source and the time of flight mass spectrometer has some advantages for the analysis of minute solid samples. This method has been introduced by Knox (Ref. 21) and perfected by Sharkey, et al. (Ref. 22). The pulse of the time of flight instrument is timed shortly after the flash of the laser. Therefore a relatively large concentration of the evaporated material can be obtained in the ion source.

Another approach has been made by Winters and Kay (Ref. 23) who used a closed, unpumped, mass spectrometer and expanded the evaporated material into the whole volume. This method does not utilize the advantages of a time of flight mass spectrometer and can be applied also with other mass analyzers. This method is less desirable since the evaporated material may condense on the walls and get lost before the analysis. The main difficulty for applying this laser/time of flight combination for the analysis of the clouds of Venus is the difficulty to introduce the sample into the ion source. The cloud particles have to be collected on a cooled solid surface which has to be brought into the vacuum through a vacuum lock. Considering the limited pumping capabilities it will take a long time to pump the system down to a sufficient low pressure to be operable. Therefore only one or very few samples can be taken during one descent of the landing probe. This may provide an integrated analysis over all cloud layers but not a detailed profile of the different layers at different altitudes. In addition a very large amount of development work would be necessary to construct a reliable instrument on this basis. Therefore, this approach is not recommended, at least at this time. Maybe at a later time, in case the previous methods have failed to detect the cloud material, this approach should be reconsidered.

SECTION V

PRE-SEPARATION OF THE CLOUD PARTICLES FROM THE AMBIENT ATMOSPHERE

If carbon dioxide can be prevented from entering the mass spectrometer ion source, a large increase of the sensitivity for the cloud materials can be expected. At the present, such a separation is hampered by the fact that little is known about the nature and size of the cloud particles. Therefore, it is suggested that on the next landing probes some special equipment is included which can determine whether the cloud particles are solid or liquid and at what temperatures the particles can be evaporated. Also an approximate determination of the size and the density of the particles for the different cloud layers would be extremely helpful. Only after these data are known it will be possible to make the optimum choice for the equipment necessary for the enrichment of the cloud material. The following possibilities should be considered.

A. Condensation on a Cold Surface

This is probably the simplest method to collect liquid particles. In order to have a cold surface available for this purpose, it would be necessary that the surface is well shielded from the solar radiation during the flight toward Venus and also well shielded during the first part of the entry in the atmosphere of Venus. By using a surface with sufficient heat capacity it should be possible to have the surface always at a much lower temperature as the ambient atmosphere during the parachute descent. Because of the expected small density of the cloud, it will take too long to obtain microscopic droplets. Therefore some kind of windshield wiper would be helpful to push the condensate of a large area together to the spot where the entrance of the capillary to the ion source is located. The temperature of the capillary must be high enough that the cloud material is at least liquid.

B. The Cyclone Type Separator

It should be possible to utilize the wind velocity around the descending probe to operate a cyclone type separator without any additional need for a motor driven fan bag.

C. Electrostatic Separator

This method depends on the assumption that the cloud particles are charged or can be charged. The preference between these methods depends on the particle size and mass, and on the thermal properties.

All these sampling methods have the disadvantage that they need a large collection time to obtain a sufficient quantity of material. Therefore only very few samples can be analyzed during one descent. It is expected that a large amount of development work is necessary to perfect the separators for this application. Therefore these approaches should be postponed for later missions.

SECTION VI

DETECTION OF FERROUS CHLORIDE WITH A MASS SPECTROMETER

The results from ground observation spectra have led Kuiper (Ref. 9) to the assumption that ferrous chloride might be present in the clouds of Venus. Therefore the literature has been searched whether somebody has produced a mass spectrum of FeCl_2 . Solid materials are generally analyzed with the spark source mass spectrometer. This method is not practical for an instrument which has to operate completely unattended because of the difficulty to prepare the electrodes. So far, there was no real need to detect FeCl_2 in analytical mass spectrometers. However, intense ion sources have been developed for isotope separators which work very well with a charge of FeCl_2 . This was reported by Freeman (Ref. 24) at the second International Conference on ion sources in Vienna. These ion sources consist of a little oven, the so-called Knudson cell, in which the small crystal of FeCl_2 is heated to about 428°C . At this temperature the vapor pressure is 1 micron. The vapor is transported by a carrier gas, usually argon, into a hollow cathode ion source. This ion source was especially designed to deliver a very large ion current. Therefore the power requirement is high and not suitable for application in the Venus instrument. However, it can be expected that the same principle can be used to supply FeCl_2 vapor to a normal Nier type ion source. In order to avoid condensation the source has to be kept at a temperature of about 400°C . This ion source, which depends on the evaporation of the sample, exhibits very large discrimination against different sample materials. If, for instance, the material in the clouds of Venus is not FeCl_2 but some other material, which may have a much lower vapor pressure, then this material could completely escape the detection. Therefore, the Knudson cell ion source combination is suitable to confirm whether or not FeCl_2 is present in the clouds and will also be suitable for some other materials, as for instance the mercury halides, which have a higher vapor pressure at the same temperature. Materials with a lower vapor pressure will not be detected.

Another method to produce ions of solid materials is by ion sputtering. The sensitivity of this method varies about three orders of magnitude from element to element which is far less than the sensitivity variations of the method previously discussed. The advantage of this method is therefore that any element which is present can also be detected. Unfortunately, no measurements with FeCl_2 were available. Since this material is a non-conductor, it was not certain that a good mass spectrum can be obtained because of charge-up problems of the sample. Such charge-up can be prevented with additional electron bombardment of the sample, but this would be an undesirable complication of the instrumentation for Venus. Although it was not the original intention to perform experimental work under this study contract, it was desirable to perform a few preliminary tests with the sputter ion source to decide whether this method would be feasible for the intended purpose.

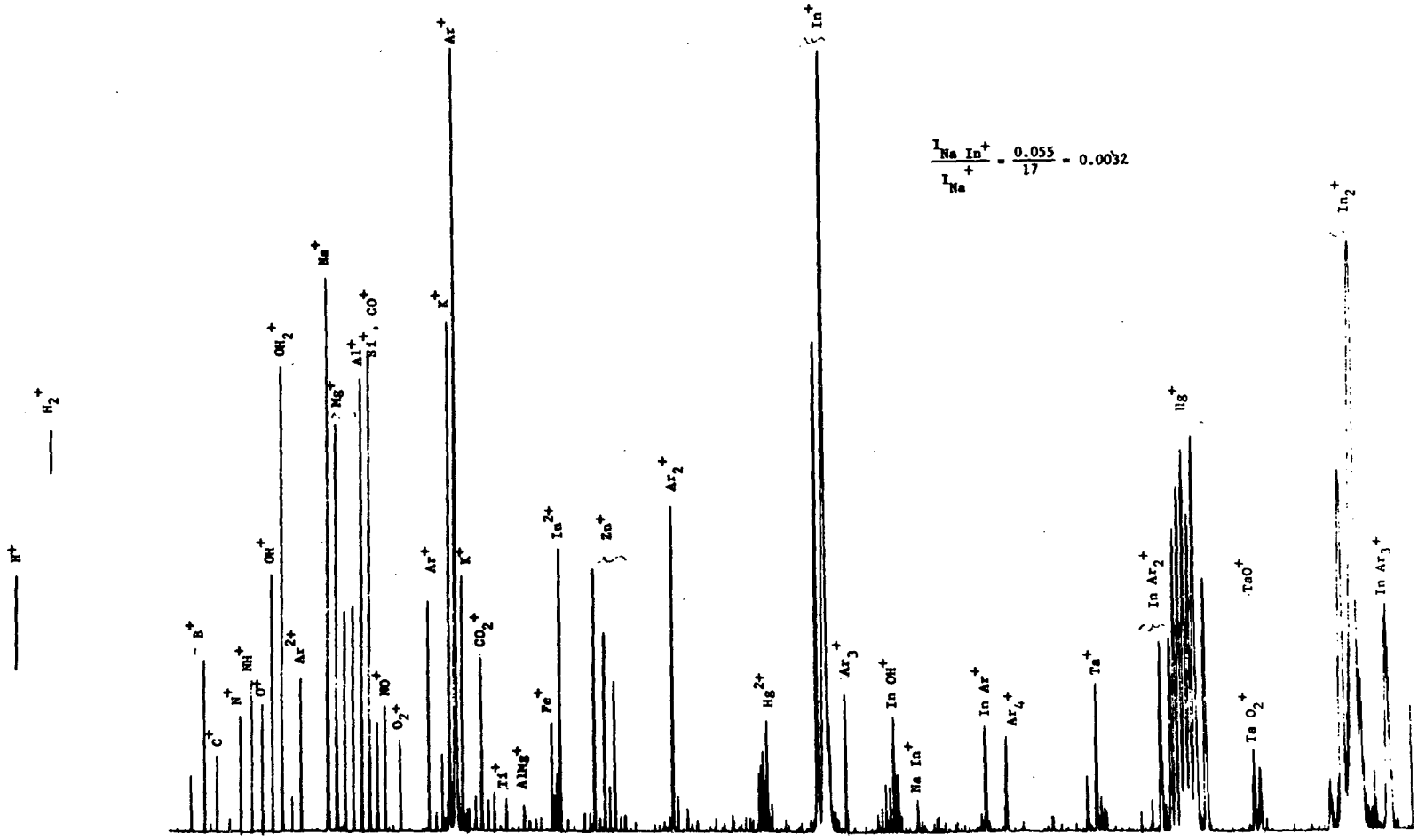
In one series of experiments the sample was prepared by evaporating a solution of FeCl_2 on a tantalum substrate. By reducing the intensity

of the primary argon beam it was possible to obtain good spectra even without charge compensation. The instrument can be adjusted to obtain either a primarily molecular spectrum or an atomic spectrum, depending on the initial energy of the secondary ions. Recording No. 26 shows a typical molecular spectrum and Recording No. 32 an atomic spectrum, both of FeCl_2 . The predominant peak in both spectra is Fe. The molecular spectra contains also intense peaks for the molecules FeCl , FeCl_2 , Fe_2Cl , Fe_2Cl_2 , and many other complex molecules of the type Fe_nCl_m . The secondary ion intensity is high and trace amounts of many contaminants are quite visible. Therefore the spectrum is rather complex and would require a good analyzer to resolve adjacent peaks. On the other hand, the relative intensity of the different molecules can be used to differentiate between FeCl_2 and FeCl_3 . The atomic spectrum shown in Recording 32 is much simpler. It contains mainly the peaks of Fe, Cl, and the substrate Ta. The remaining few peaks are quite small and represent the normal contamination of most materials. In this case, a mass analyzer with limited resolution would be adequate.

The preparation of the sample would be relatively simple. The target substrate, either tantalum or some other suitable material, would be exposed to the atmosphere of Venus during the parachute descent of the instrument. Cloud particles will impinge on the target with a velocity of approximately 100 meters per second, and probably be deposited on the target. Thereafter the target has to be brought into the mass spectrometer through a vacuum lock.

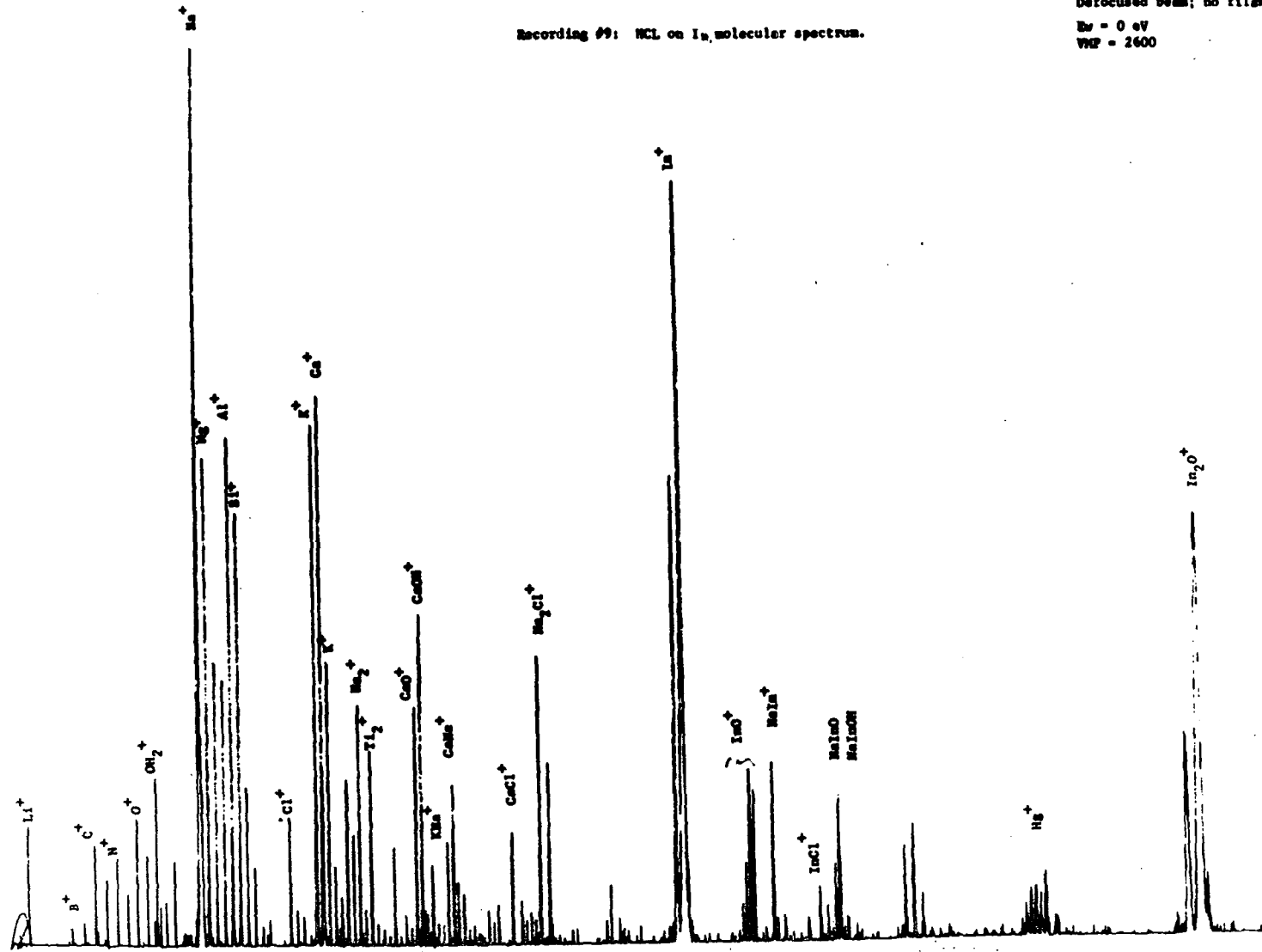
Another widely accepted assumption is that the cloud particles consist of diluted hydrochloric acid. It would be desirable that the same method could be used to detect hydrochloric acid. If the target material does not react with hydrochloric acid, then the liquid would evaporate after the target has been brought into the high vacuum of the mass spectrometer. However, if we employ a substrate material which reacts with hydrochloric acid then the resulting chloride could be detected in the same manner as previously ion chloride. For a preliminary experiment in this direction, indium has been chosen because it is unlikely that indium is present in the atmosphere of Venus. Recording 8 shows the molecular spectrum of "clean" indium which is rather complex because of numerous impurities. Recording 9 was obtained from the same target material on which the diluted HCL solution has been placed. The surprising result is that a large Na_2Cl peak appeared whereas the In Cl peak is relatively small. The atomic spectrum on Recording 16 is again much simpler and contains a fairly large chlorine peak. The large intensity of sodium, potassium and calcium is not surprising since the secondary ion yield for these elements is extremely high. From these preliminary experiments it cannot be decided whether the sodium chloride was a contaminant of the hydrochloric acid or was formed in the target by reaction of the sodium contamination with pure hydrochloric acid. This decision would require much more experiments with extremely pure chemicals, which is beyond the scope of the present contract.

The preliminary experiments which have been described indicate that the ion sputter method would be useful for the analysis of the cloud particles on planet Venus. However, considerably more experimental work would be necessary to establish the optimum operating conditions of such a instrument.



Recording #8: In substrate, molecular spectrum.

13:05
 Opt on In Ar⁺
 Foc 5
 (E_w = 0 eV)

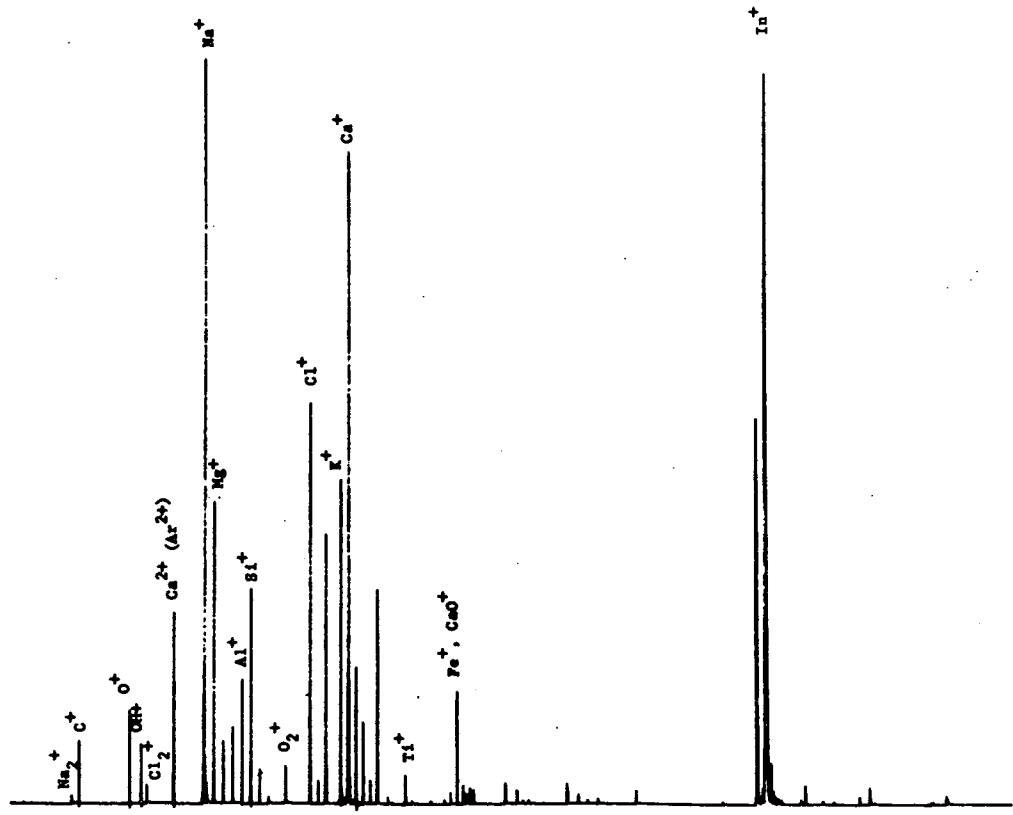


Recording #9: NCl on In_2 molecular spectrum.

13:53
In - NCl(0.002M)
Defocused beam; no filament
E₀ = 0 eV
VHP = 2600

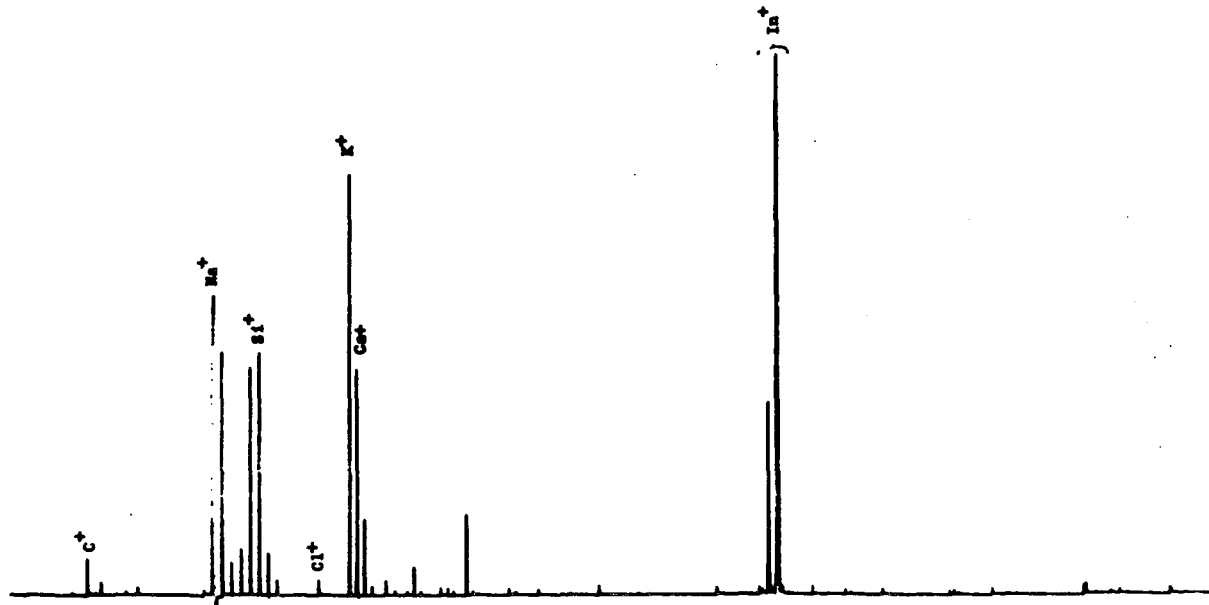
Ev = 100 eV
11:12

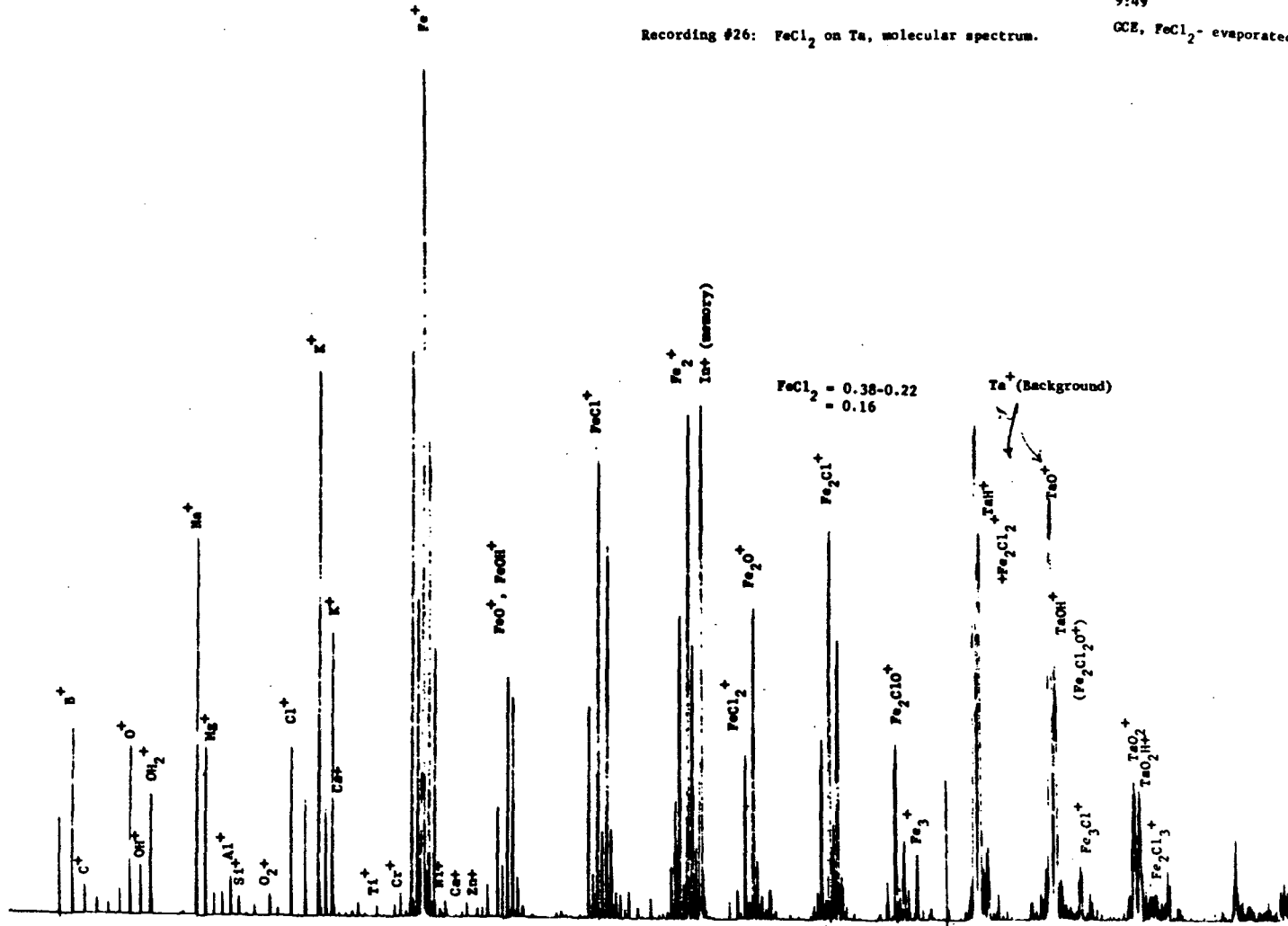
Recording #16: HCL on I_n atomic spectrum.



12:27
100 eV
Moved off residue

Recording #20: In substrate, atomic spectrum.

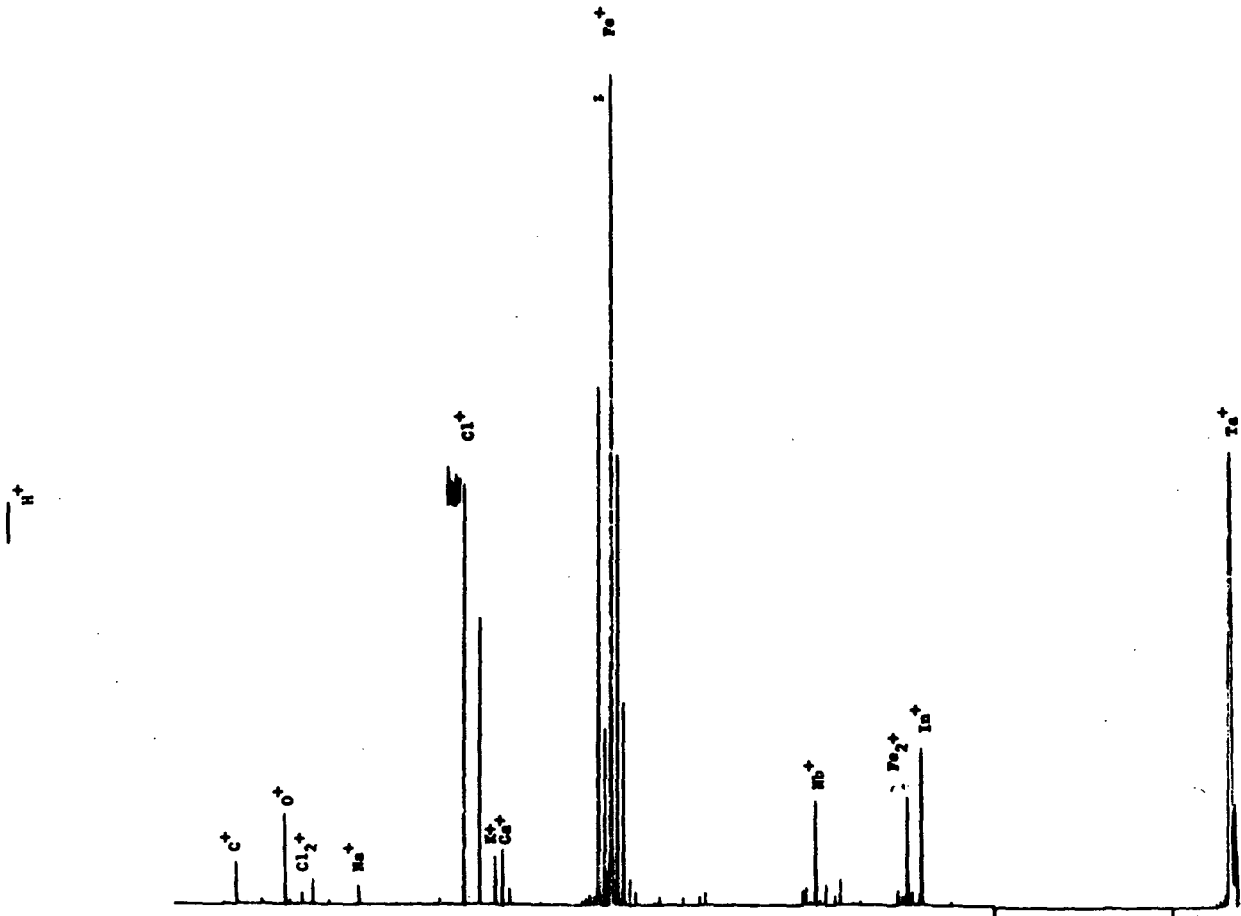




9/22/72
 9:49
 Recording #26: FeCl₂ on Ta, molecular spectrum.
 GCE, FeCl₂ evaporated.

FeCl₂ X tal
11:27
CE
100 eV

Recording #32: FeCl₂ on Ta, atomic spectrum.



SECTION VII

RECOMMENDATIONS

For the first instrument to be used to analyze the cloud materials, a mass spectrometer shall be used which has already been developed and would be suitable for this purpose with only minor modifications. Such instruments are the magnetic mass spectrometer and the quadrupole mass spectrometer. Higher electron energies should be used in the ion source in order to fragment the large mercury halide molecules and to produce doubly charged mercury ions. This will eliminate the need for an extensive mass scale. A heated inlet system with several leaks which can be closed when the probe enters the lower atmosphere shall be used since it has the advantage that if one of the leaks should be blocked by a solid material the others may still be useful. Every attempt should be made to increase the sensitivity of the instrument for trace impurities. This requires an ion source of high intensity and an analyzer of sufficiently large dimensions to prevent losses of the ion beam on the walls. The very high intensity of the carbon dioxide beam will produce secondary ions in the gas of the analyzer which contribute to a disturbing background. This background has to be suppressed to permit the detection of trace impurities. Retarding field arrangements before the electron multiplier are only moderately effective. The best way to suppress the background is by use of a tandem type mass spectrometer. Weight considerations would exclude the use of a magnetic type mass spectrometer for this purpose. The tandem arrangement of a quadrupole or monopole mass spectrometer would increase the weight of the whole system only moderately and is therefore worth considering. It is expected that better suppression of the background can be obtained with the monopole arrangement, because the aperture between the two monopole sections is small. In contrast, the aperture between the two quadrupole sections has to be wide in order to achieve a good performance of the instrument. It is suggested that laboratory type tandem mass spectrometers of the quadrupole and monopole type should be built to test the actual performance. Immediate work should be concentrated on these problems before further work on the separation of the cloud particles from the ambient atmosphere shall be started.

REFERENCES

1. Avduevsky, V.S., M. Ya. Marov, M. K. Rozhdestvensky, N. F. Borodin and V. V. Kerzhanovich, "Soft Landing of Venera 7 on the Venus surface and preliminary results of investigations of the Venus atmosphere", J. Atmospheric Sciences 28, 263, 1971.
2. Marov, M. Ya, V. S. Avduevsky, M. K. Rozhdestvensky, V. V. Kerzhanovich, N. F. Borodin and O. L. Ryabov, "Results of the Venus atmosphere measurements made by the landing station Venera 7", Space Research XII, p. 281, 1972.
3. Vinogradov, A.P., Yu.A. Surkov, B.M. Andreichikov, O.M. Kalinkina, and I.M. Grechishcheva, "Chemical composition of the Venus atmosphere", Space Research XI, 129, 1971.
4. Kolosov, M. A., O.I. Yakovlev, G. D. Yakovleva, and A. I. Yefimov, "Radiowave fluctuations and refraction coefficient variations in the atmosphere of Venus", Space Research XI, 148, 1971.
5. Rea, D. G., "Composition of the upper clouds of Venus", Rev. Geophysics and Space Physics 10, 369, 1972.
6. Rasool, S. I., and R. W. Stewart, "Results and interpretation of the S-band occultation experiments on Mars and Venus", J. of Atmospheric Sciences, 28, 869, 1971.
7. Gold, T., and S. Soter, "Atmospheric tides and the 4 day circulation on Venus", Icarus 14, 16, 1971.
8. Irvine, W. M., T. Simon, D. H. Menzel, C. Picoos, and A. T. Young, "Multi-color photoelectric photometry of the brighter planets", Astron. J. 73, 807, 1968.
9. Kuiper, G.P., "Identification of the Venus cloud layers", Commun. Lunar Planet Lab. 6, 229, 1969.
10. Cruikshenk, D.P., and A.B. Thomson, "On the occurrence of ferrous chloride in the clouds of Venus", Icarus 15, 497, 1971.
11. Plummer, W. T., "The Venus spectrum: New evidence for ice", Icarus 12, 233, 1970.
12. Schorn, R. A., and L. G. Young, "Comments on 'The Venus spectrum: New evidence for ice'", Icarus 15, 103, 1971.
13. O'Leary, B., "Venus halo: Photometric evidence for ice in the Venus clouds", Icarus 13, 292, 1970.

Preceding page blank

14. Lewis, J.S., "Ice clouds on Venus?", J. Atmospheric Sciences 27,333, 1970.
15. Fukuta, N., T. L. Wang, and W. F. Libby, "Reply", J. Atmospheric Sciences 27, 334, 1970.
16. Donahoe, F.J., "Is Venus a polywater planet?" Icarus 12, 424, 1970.
17. Lewis, J. S., "Geochemistry of the volatile elements on Venus", Icarus 11, 367, 1969.
18. Oboukhov, A.M., and G. S. Golitsyn, "Some problems of atmospheric physics for terrestrial planets", Space Research XI, 121, 1971.
19. Lovelock, J.E., P.G. Simmonds, and G. R. Shoemake, "The palladium generator - separator - a combined electrolytic source and sink for hydrogen in closed circuit gas chromatography", Anal. Chem. 42, 969, 1970.
20. Herzog, R., "Mass Spectrometer for D Region Studies. Part 1: Laboratory Tests" Final Report, Contract NASW-1314,GCA-TR-71-1-N (1971)
21. Knox, B.E., "Mass spectrometric study of the laser-induced vaporization of Selenium and Various Selenides" Advances in Mass Spectroscopy, Vol. 4, 491, 1968.
22. Sharkey, A.G., A.F. Logar, R.G. Lett, "Laser-time-of-flight mass spectrometer studies of sorbed species and surface reactions", 19th Annual Conf. on Mass Spectroscopy, 331, 1971.
23. Winters, H.F., and E. Kay "Gas analysis in films by laser induced flash evaporation and mass spectrometry", 18th Annual Conf. on Mass Spectroscopy, B277, 1970.
24. Freeman, J.H. and G. Sidenius, "Technology and chemistry of heavy ion sources", I.C.I.S.-2, Vienna, 1972.