

AN APPLICATION OF GAS CHROMATOGRAPHY TO PLANETARY ATMOSPHERES

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DR. VANCE OYAMA: I guess the best way to ~~start~~ on a subject that is relatively new to the physical world but has been practiced for years in the chemical world, is to start with something that people can easily relate to. Let us take a Coke bottle and shake it up. When it is cold, very few bubbles occur in that Coke bottle. When you take this Coke bottle and you shake it up when it is warm and open the cap, out comes your Coke in a sudden burst of energy. Essentially, I am talking about the process of partition in a two phase system, a gas and a liquid.

In the liquid system, you have dissolved carbon dioxide in the above case. When the dissolved carbon dioxide escapes from the liquid, it causes the ebullition.

In gas chromatography, the same kind of phenomena occur except not so violently. In a system in which you may have stationary phases of liquid, semi-liquid, a polymer or a solid as one phase, and in the gas phase a dissolved solute, the gas tends to move into the solid or the liquid phase until there is an equilibrium set up between the gas and the liquid phase in which the concentration in both phases is a function of the parameters of the system - temperature, phase, gas, etc.

Now suppose that you transfer this gas in the head space to another portion of this system in which you have the stationary phase, but have no solute gas. That gas then re-equilibrates with the new stationary phase and it sets up this particular partition coefficient. This is essentially like saying that there is a certain concentration in the head space and a certain concentration in the liquid phase. Now consider a movement of a stream of gas such as helium moving across the stationary phase. The solute gas tends to move out of the stationary phase and move into the gas phase. The solute gas in the gas phase moves down into the liquid and similarly, along the train, as you can see. If a gas has a strong affinity for the liquid, it will be retained

and slowed down in the process; whereas a gas that has limited affinity for the liquid phase will move along the train very rapidly. There is a separation of the two phases.

Figure 3 - 47 is an example of the process I am talking about. On top we have a column coated with a stationary phase of some sort, that has different affinities for X and O molecules introduced into it. A carrier gas, such as helium, drives the binary gas mixture to the right. This gas plug moves along and in the second display the components begin to separate. In the ideal system, the components are separated and you are ready to sample. You want a detector at the column outlet that is able to distinguish from the carrier system - a particular peak has arrived - and is able to quantitate it over a large dynamic range. This is, in essence, gas chromatography. It is a very simple process.

Now how does this differ from mass spectrometry, which is the other mode of composition analysis? Gas chromatography is obviously a high pressure system. It is a high pressure system that can take a high pressure gas, introduce it into the system, and come out with an answer. It does not require a pump. All it requires is some pressurized gas source.

How, again, does this differ from the mass spectrometer? The mass spectrometer impels electrons against the molecules of interest these molecules are fragmented and ionized imparting a characteristic to it that allows fractionation by an electric field and/or a magnetic field. The difference is that the gas chromatograph separates components without changing the structures. The retention time helps to identify the molecule.

Now, the resolution capability of the gas chromatograph will depend primarily upon what you want out of the system. If you want to measure something of low molecular weight, you devise or

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STATIONARY
PHASE

CARRIER GAS

STATIONARY
PHASE



OOO
OXOXOXOX
XOXOXOXO
OXOXOXOX

XXXXXXXXXX

T₁



OXOXOO
XXOXOOO
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T₂



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STAGES OF CHROMATOGRAPHIC SEPARATION

Figure 8-47

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tailor-make your system to get the fastest analysis consistent with the degree of resolution required for the gas species likely to be present. Say you want to measure a cc and you want to do it rapidly, you design a particular system to do just that. The gas chromatograph can be ultimately made to do all the gas analyses one requires. For example, the gas chromatograph can separate isotopes. Contrary to belief, the reason that these processes have not been performed routinely on a laboratory scale is simply because the conditions for these analyses are not usually attainable. For example, it is possible to separate molecular hydrogen from HD by running the column of, say, aluminum oxide at temperatures of about minus seventy degrees centigrade. If you want to take a spacecraft and go through space, cool it down, and run these columns at the temperature, you can make these kinds of separations. So, it is really what the particular people want out of the system that we can design to.

In the case of the Viking experiment, a gas chromatographic system is provided which measures the head space in a chamber. We hope to find biological activity present there.

The system as shown on Figure 8-48 consists of a chamber, which provides the head space. Soil is introduced into the chamber and gas and liquid nutrient added. A sample of the head space fills the sampling system by utilizing the martian ambient pressure. The greater head pressure of the chamber allows us to move gas through the sampling assembly by appropriate valve actuations. The sampler then injects into the carrier stream the sample of gas. This is a volumetric sample and is not something that is measured because of the capillary flow. Having a volumetric sample allows us to estimate the concentration of every gas that is in that volume provided pressure is known and all gases that enter the column enter the detector.

In the Viking GEX a thermoconductivity detector - thermistor heads - are used. The helium flow in the reference leg going

GAS EXCHANGE EXPERIMENT

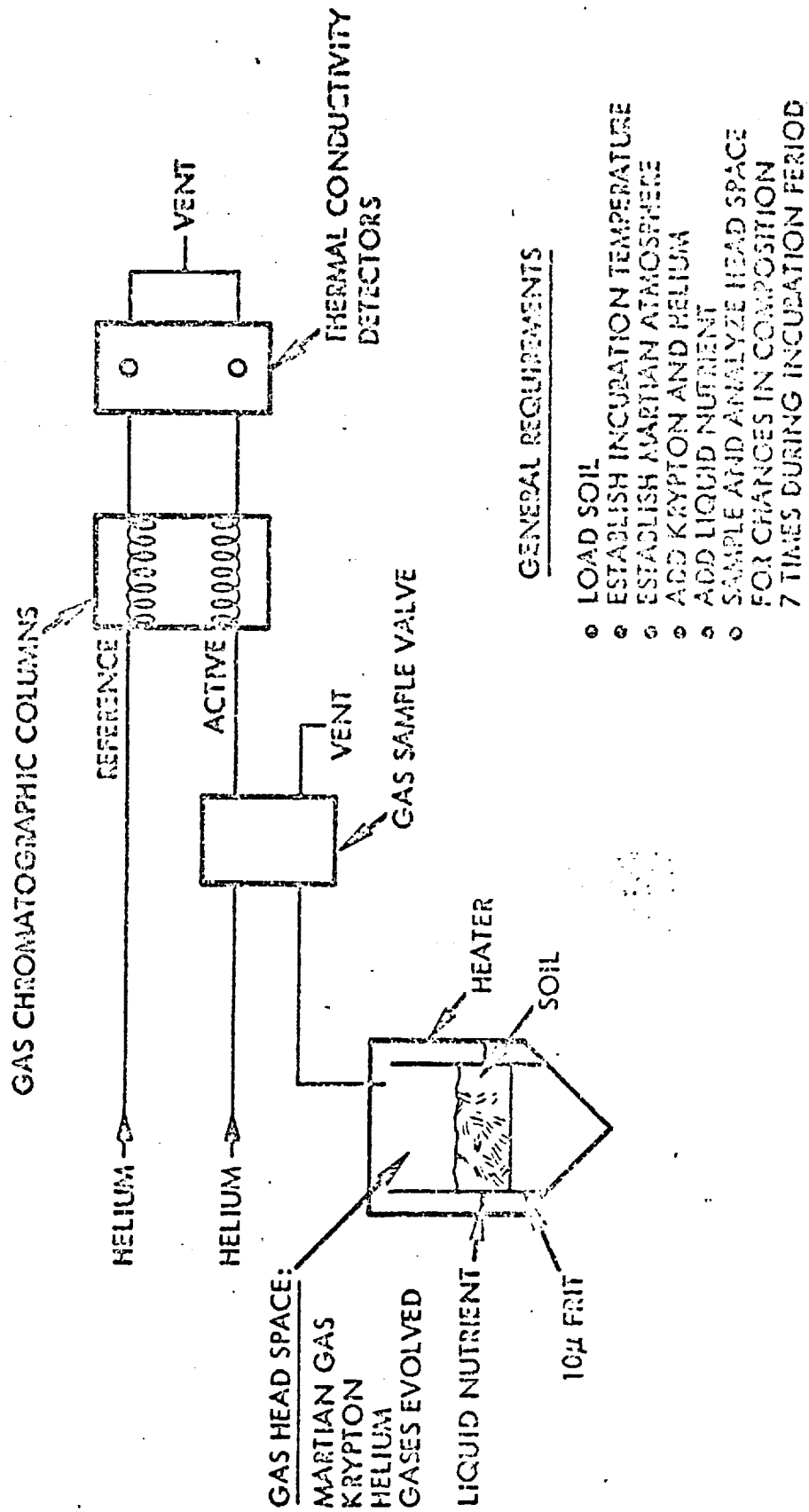


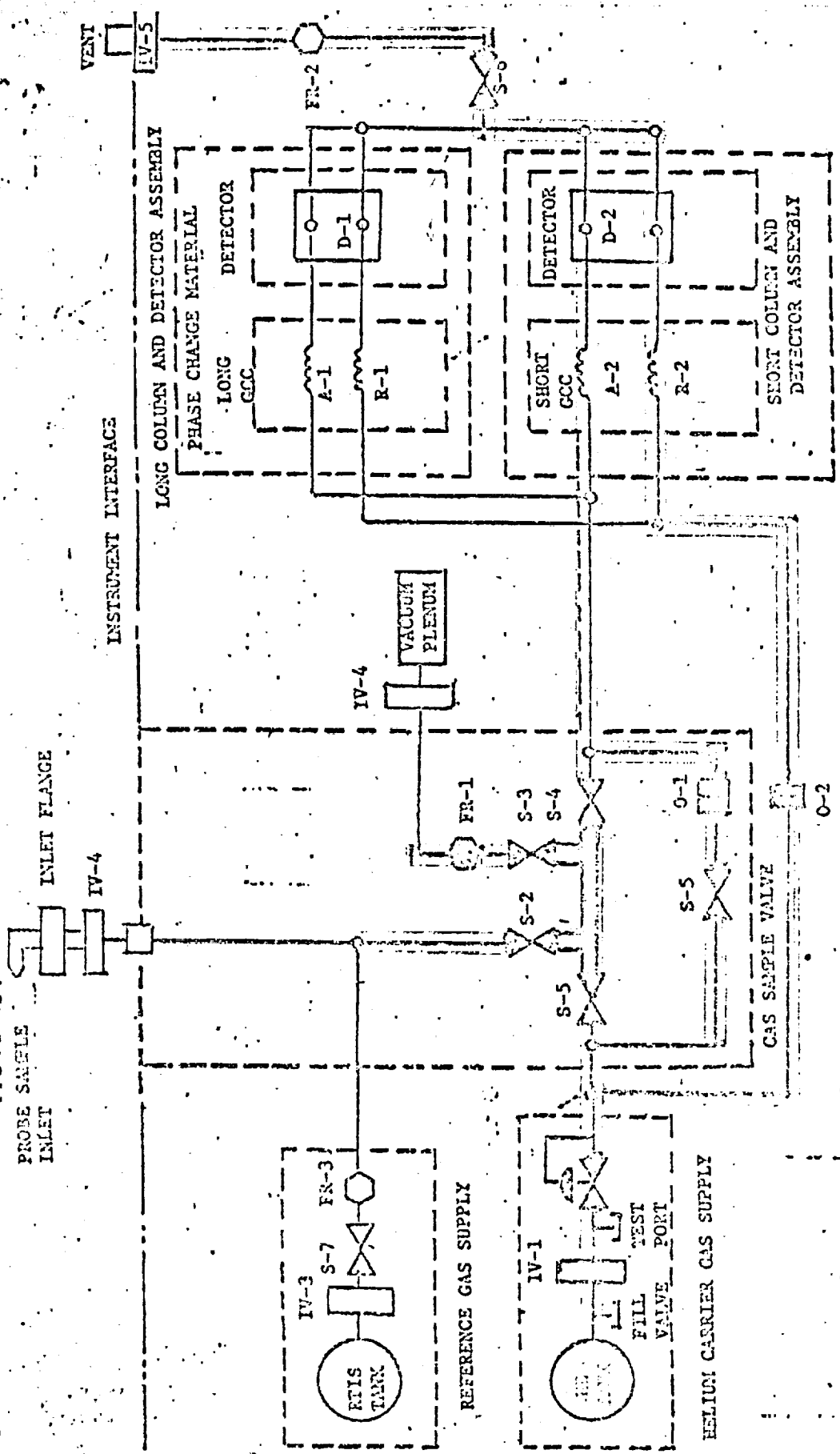
Figure 8-48

through an identical column allows us to balance temperature fluctuations which would normally make a thermister type detector unstable. With this system we are able to separate such gases as hydrogen, nitrogen, oxygen, methane, krypton, and carbon dioxide. The reason we have put krypton into this system is to provide an internal standard to the entire system. The internal standards allow us to make corrections of the time in which a gas arrives at the detector to compensate for changes that might have occurred in the system. From this exact measurement of krypton, we are able to get relative retention times. These retention indices are required if we are to define a particular substance in the head space.

The reason we require this is because the thermoconductivity detector is basically a cathodic detector, it is a universal detector. It measures everything that has thermoconductive properties that differ from the carrier gas, helium. Since the Viking GEX utilizes only one way of identifying the substance, i.e. thru its retention index, we must be very careful to establish a standard known substance that the retention time is relative to. We have provided krypton as our internal standard.

Figure 8-49 is a schematic of the Pioneer Venus gas chromatograph and because of the basic economy of the mission, emphasis was placed on adopting Viking GEX features. We incorporated the thermister systems to monitor the output of two pairs of columns. We have a single sampling device which allows Venus atmosphere to pass through the sample loop into a plenum continuously during descent of the large probe. The plenum is the simple, enclosed volume of about thirty cm³. Before entering the atmosphere, the thermoisolation valve is open, exposing the sampling system to the atmosphere of Venus.

Now, the use of two columns in the Venus probe emphasizes the concept of tailor making a system for a particular job. Two columns were required to separate the wide range of gases likely



WUGCIA FLIGHT DESIGN SCHEMATIC

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Figure 8-49
VIII-94

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NOTES

to be in the Venus atmosphere and in addition there was a complementary need to support the mass spectrometer.

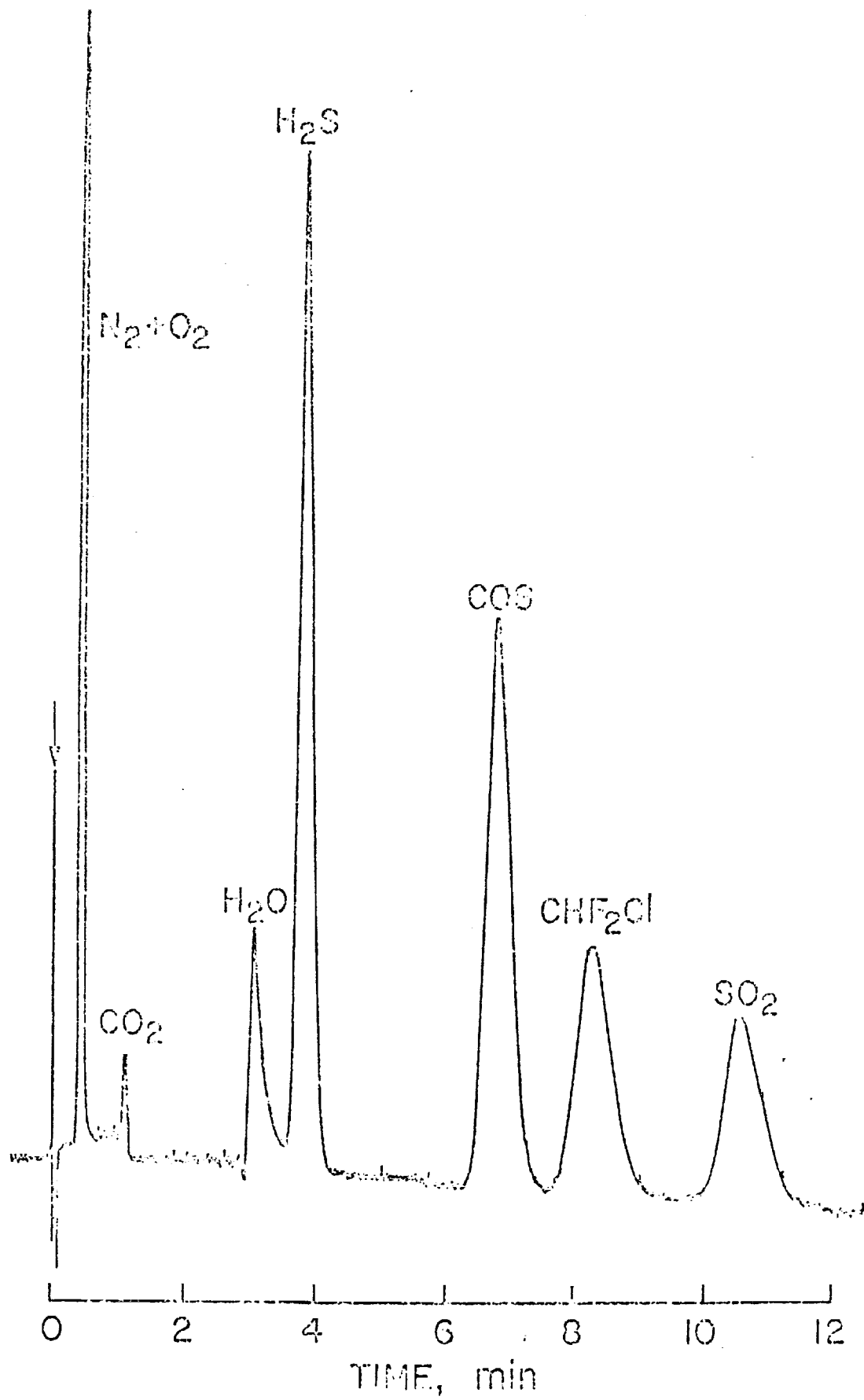
As the previous speakers have pointed out, in order to get a good analysis of a particular sample gas, you break it down so you can see its fragments. Now, a number of gases are associated together, the resulting fragmentation patterns with coincidental M/e could confuse the analysis. It is for this reason that we felt that it was necessary for us to develop columns which will allow us to make separations that could pose a problem for the mass spectrometer. Therefore, for the short column in this assembly, we designed the column to make the separation of carbon dioxide, hydrogen chloride, water, hydrogen sulfide, carbonyl sulfide and sulfur dioxide, (Figure 8-50). The long column was designed to separate such gases as neon, hydrogen, nitrogen, oxygen, argon, carbon monoxide, methane and krypton (Figure 8-51).

In the long column, not all the bases introduced will traverse the column during the descent period but are retained in the columns. These gases on shorter columns and/or higher temperatures could very well be detected in the period of analysis.

If you will note, although we have tailor-make the columns to make these separations, there are plenty of spaces for unknown objects to appear in our particular system. The virtue of GC in the low molecular weight range is the fact that there is only a limited number of low molecular weight substances. Consequently, we can provide for any vacancies that might occur in our particular system.

Because the major component in the atmosphere of the planet Venus is carbon dioxide, the question is could one really detect the other minor and trace components of interest? Figure 8-52 shows that at 10 bars we have this immense peak for carbon dioxide (top chromatogram), upon which these various components at relatively low levels are detectable.

Now, how do we go to the outer planets? If we take a look at the planet Jupiter, or Saturn, or any of these larger planets, the major components may be helium and hydrogen. If one assumes that

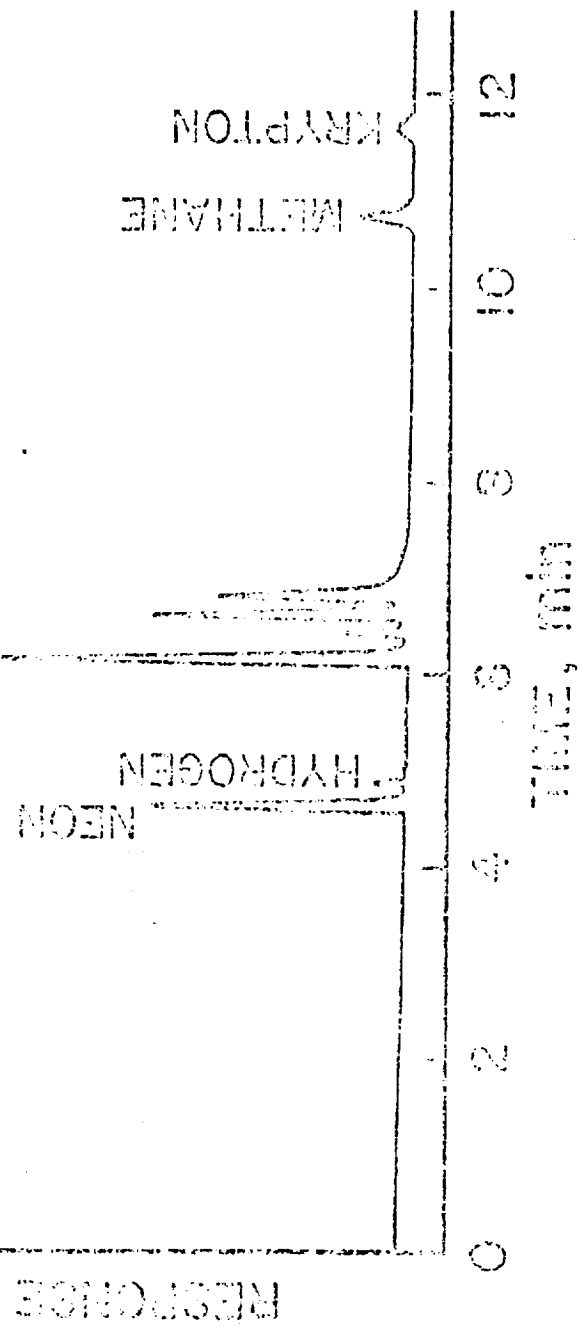


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Figure 8-50

COLUMN: 51 ft x 0.040 in.
 PORAPAK N
 TEMP 20°C
 FLOW 55 cc/min

NITROGEN
 OXYGEN
 ARGON
 CARBON
 MONOXIDE



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CHROMATOGRAPHIC SEPARATIONS ON
 POROUS CHROMATIC HYDROCARBON COLUMNS

Figure 8-51
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Chromatogram of various gases
at the 1000 PSI level in CO₂.

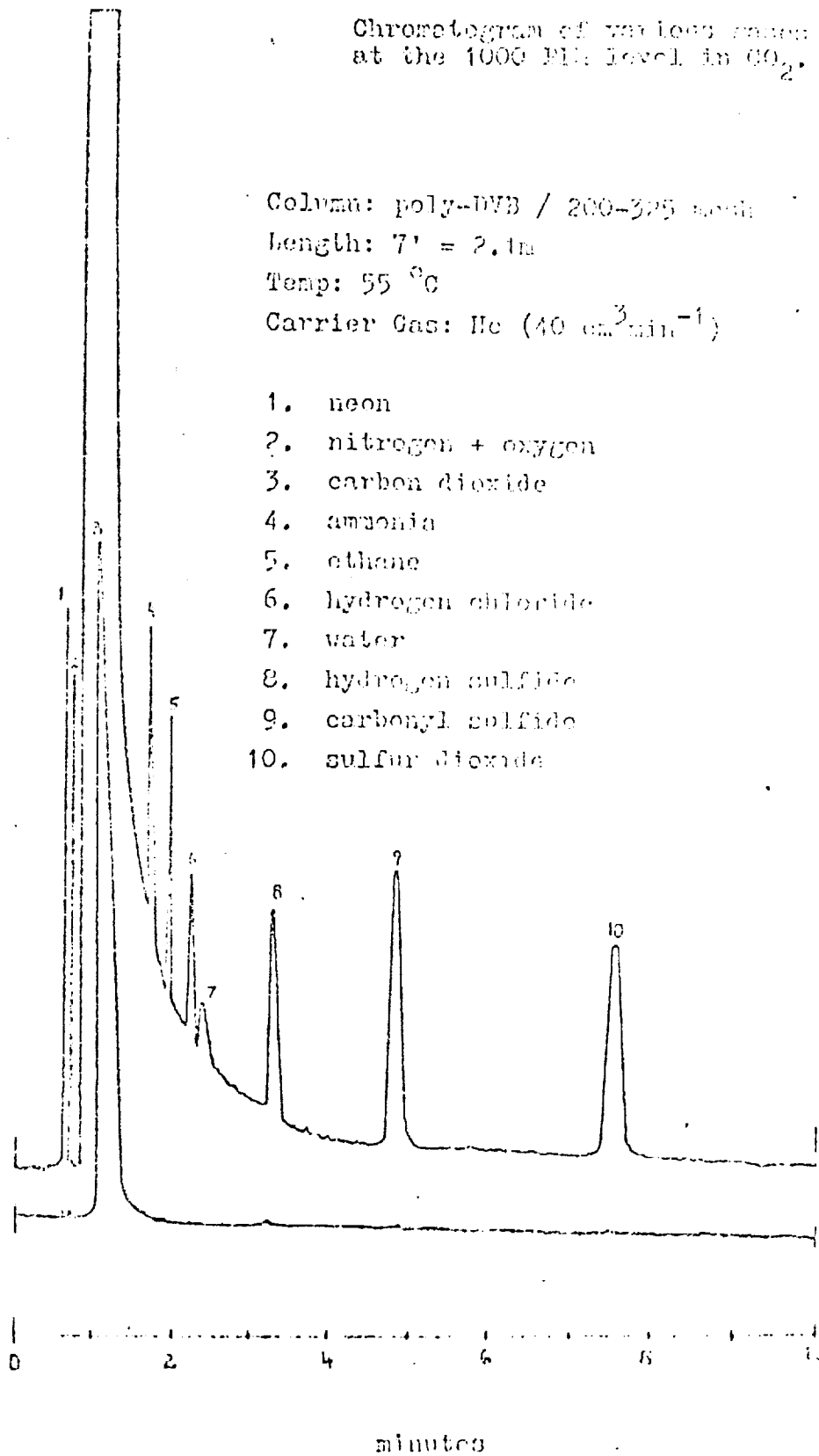
Column: poly-DVB / 200-325 mesh

Length: 7' = 2.1m

Temp: 55 °C

Carrier Gas: He (40 cm³ min⁻¹)

1. neon
2. nitrogen + oxygen
3. carbon dioxide
4. ammonia
5. ethane
6. hydrogen chloride
7. water
8. hydrogen sulfide
9. carbonyl sulfide
10. sulfur dioxide



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HOYES

Figure 8-52

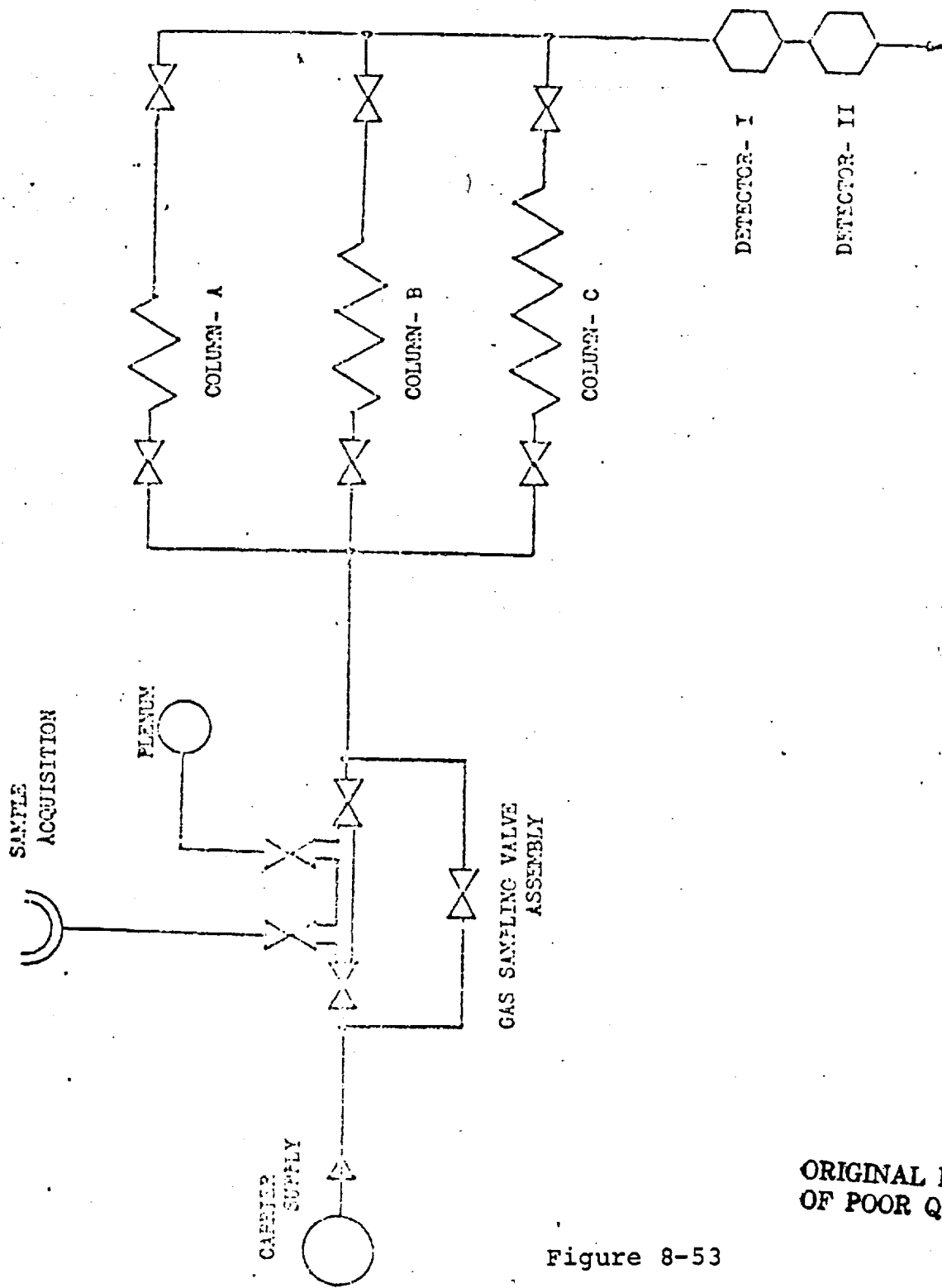
VIII-98

C-9

these are the major components and they represent 95% of the atmosphere, if you have a known volume, you have a known pressure that you measure during that sampling interval and you know what the temperature of that particular sampling system is then, simply by the gas laws, it's easy to compute what remains in your system. So, it is possible to measure hydrogen and assume the concentration of helium simply by using the helium carrier system. It is not necessary to measure all the components in such a system.

The systems we were talking about are systems that have already been built or are being built. We have talked about the carrier gas supply which is something that is on the Viking mission. I have not talked about the regulator but there is a regulator. We have the sampling gas assembly system and, of course, these valves are all miniature latching solenoid valves that are space qualified. In Figure 3-53, is a schematic of an outer planets gas chromatographic system. It has additional valves and three separating columns. We have lost the column pairs here because what we are now proposing for the outer planets are detectors which are not influenced by temperature and pressure changes and no reference flow is required. Basically, we are talking about the inclusion of ionization detectors. What are ionization detectors? Ionization detectors are detectors which utilize radioactive sources such as strontium 90 or nickel 63, in an electric field sufficient to ionize gases of interest in the carrier stream. These radioactive sources provide electron current which is on the order of about 2×10^{-9} amps upon which currents of 3 to 4 orders of magnitude can be read.

With this steady background, one which provides for a fairly constant flow of electrons, one can essentially excite molecules and ionize them by providing a variety of electric fields. With high electric fields, one can cause a great agitation but it is not really important in this case because we don't care how much we fragment, we only care that we get a signal; and that this signal has a relatively useful range. We have sequenced detec-



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Figure 8-53

tors in series to compensate for a very important program. The compensation is the fact that in the Pioneer Venus mission, we have deliberately required that the retention index be the parameter of interest because we decided to go with the economy of the thermistor detector system.

Because we have taken that turn, we can now re-analyze the situation. We can see that if we can apply, in tandem arrangement, two detectors of unique quality which depend upon independent physical properties, we can therefore qualitatively identify a pure substance, analogously to a mass spectrometer's dependence upon fragmentation patterns, except that we would require some other technique in which high pressure could be used. The ionization detectors are the things that I am referring to.

With this type of system, we can now coast to the outer planets. As the temperature rises entering the atmosphere, the columns equilibrated at the colder cruise temperature will follow. We can take advantage of this rise in a very clever way. We can use the same column material, or various column materials, in various lengths. We can have a long column, a medium column, and a short column. The column lengths will then provide us with the kind of approximation which will give us the answers on the integral components, that is, the ones that are in the particular atmosphere.

For example, at the high altitude, the main interest might be the very light gases - helium and hydrogen, maybe argon and nitrogen. We can expect to make separations of these components with a long column very adequately.

The next sampling point is taken at a lower altitude. The sample is introduced into the medium sized column. Again, we will get a separation. Now, however, the light components come out unresolved. Their resolution will not be as good, but the moderate gases will come out and they will be nicely separated. Residual gases remaining in the long and medium columns remain trapped.

For the last case, we could use a very short column. Meanwhile, the temperature of the probe has gone up to, say, seventy degrees centigrade. This allows us to make very nice separations of such polar gases as water, carbonyl sulfide, or whatever you want to consider in this particular system, even such gases as acetylene and benzene, if these may be there.

What I have talked about here is the system which we think is quite flexible, allows us to work with a high pressure system, and allows us to take volumetric samples and make analyses. One thing I want to point out is this sample acquisition system.

The sample acquisition system here is one in which there is dynamic flow. If you have dynamic flow, you have many components in this gas flow making contact with absorbing surfaces. If you only take in a very small portion of the gas molecules, like when you are talking about a vacuum system, then you have a big problem. In the system described, we are talking about a large number of molecules, which are in equilibrium with all of these surfaces. Virtually, we have a non-discriminating sampling device.

Figure 8-54 shows the detectors that we have in mind, which we are presently studying. There are about twenty-five more classes of detectors that could be added. Mainly, these are ionization detectors and they all have their particular virtues. The interesting part here is that the thermoconductivity detector that we have called the nominal one, relative to some sensitivity scale, (and that would be equivalent to five parts per million of nitrogen detection at ten bars, something along that order), you can see the kind of sensitivity increases that are afforded by an ionization detector.

As you can see, the physical properties we can talk about are various. We can take these combinations, and we have, essentially, an orthogonal approach to qualitatively identifying a particular substance. Two detectors in series, in which one

G. C. DETECTORS

DETECTOR	CARRIER GAS	RESPONSE TO PHYSICAL PROP.	LINEARITY	SENSITIVITY (REL. TO THERM.)
CROSS-SECTION	He	CROSS-SECTION FOR IONIZATION	4	0.1
DISCHARGE (RF, DC)	H ₂	NON DISCRIMINATING	4	0.1
THERMISTOR	ANY	THERMAL CONDUCTIVITY	4	1
DIELECTRIC	He	DIELECTRIC	4	1
ELECTRON MOBILITY	He	NON DISCRIMINATING	2-3	10
ARGON IONIZATION	Ar	IONIZATION AT LESS THAN 10.6 eV	5	100
PHOTOIONIZATION	He(RF)	UV ABSORPTION (ALL GASES)	4	10 ³
ELECTRON CAPTURE	Ar	ELECTRON AFFINITY	4	10 ³
HELIUM IONIZATION	He	NON DISCRIMINATING	3	10 ⁴
ELECTRON IMPACT*	He	NON DISCRIMINATING	6	10 ³
FIELD IONIZATION*	He	RELATIVE TO FIELD STRENGTH	6	10 ⁶

Figure 8-54

sample is traversing, will obviously give you answers which are fairly respectable.

SESSION IX
SPECIAL SUBSYSTEM DESIGN PROBLEMS

Chairman: Ronald Toms
Jet Propulsion Laboratory

MR. VOJVODICH: As usual, we saved the best until last. This morning's session, Number IX on Special Subsystem Design Problems, will be chaired by Ron Roms from the Jet Propulsion Laboratory, and his session will deal mainly with the area of planetary quarantine. He does have a couple of papers that fall in a specialized category on radiation effects as well as thermal control. So, without further delay, and hoping that this morning maybe we can stay on schedule and possibly start our afternoon session a little early, let me introduce Ron.

MR. RONALD TOMS: Thank you Nick. As Nick said, this morning's session has, perhaps an emphasis on planetary quarantine. It was kind of a catch-call session for those special problems that come up in the design of probes, and in designing the overall mission that might be very important to be thinking about because of their impact, in particular, on cost.

Planetary quarantine is one that would have a serious impact on cost and complexity if we have to adopt it. It still isn't clear, of course, whether we need planetary quarantine on the outer planet probes. NASA Headquarters has been talking a great deal about having a big get-together to discuss "the planets of biological interest." That's supposed to be a topic of a seminar that was to be held in mid-August. But the latest I have on it is that they haven't picked a date yet and it is not certain that that particular seminar will ever be held. The problem has been to try to get people like Horowitz, Liederberg and Carl Sagan all available at the same time to get together. A decision is eventually going to have to be made on whether we have to adopt planetary quarantine for the outer planets.

I will now call upon our first speaker, Mr. Al Hoffman of JPL, for an overview of planetary quarantine.