NASA Grant #NGR-52-083-002

to the

College of the Virgin Islands

for

Research in the Optimization of Separator Sub-systems

for GC/MS Life Detection Instrumentation

ANNUAL REPORT

November 15, 1969 - July 15, 1970

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Caribbean Research Institute Project #29

FINAL REPORT

1969-1970

NASA Grant #NGR-52-083-002

CRI Project #29

Effort on this grant from November 15, 1969 to July 15, 1970 was expended in two major areas.

I. Improvement of Instrument Performance

For several months difficulty had been experienced with strain-cracks in the glass inlet system resulting, on several occasions, in catastrophic air leaks. These air leaks, plus long term use of the mass spectrometer, resulted in greatly reduced sensitivity of the electron multiplier. It was decided to make a major overhaul of the mass spectrometer assembly and to design a stainless steel inlet system. Late in November a trip was made to California for conferences with Finnigan Instruments and Specialty Instruments. The required parts for the overhaul (ion gauge, ion source and electron multiplier) were obtained from Finnigan

Instruments along with instructions for their installation. Working with Specialty Instruments Co., a stainless steel inlet system was designed and an all stainless valved bypass system was devised for direct evaluation of separator performance. This system is shown in Fig. 1A. It allows a calibrated sample to flow thru a metering valve either directly into the MS or thru the separator under test and thence into the MS. This test system eliminates errors due to changes in flow systems, re-establishment of exact temperature control points, leak characteristics of tubing fittings, etc. This system enables the direct measurement of separator enrichments, providing a means of evaluation of various types of units. This test system and the stainless, inlet-system were placed in order and installed early in 1970.

II. Separator Test Program

Three types of separators were included in the test program: a glass Ryhage type, a silver foil

Blummer type and a Varian hydrocarbon transfer membrane type.

A. Ryhage Type Separator - This model had the following mechanical layout

Inlet Nozzle - 0.04 mm.
Outlet Nozzle - 0.09 mm.
Nozzle Separation - 0.20 mm.

To test this separator a calibrated sample consisting of 20% each of He, Ne, Ar, Freon 14 and Xe was used. The separator was inserted in the test system as shown in Fig. 1A and two types of measurements made.

Direct Measurement

Valves V, S and T are opened, P closed and the system evacuated. Valves V and S are closed. Valves T and M are opened and a background spectra taken on the system. The metering valve P is opened to allow the sample mixture to pass directly into the mass spectrometer and is set so that the MS pressure is in the range of optimum sensitivity (2x10-5mm.). A spectra is then recorded and peak heights of the individual components measured.

Separator Measurement

Valves M and P are shut, valves V and S opened and the test system evacuated. Valve T is shut, M opened and a background run. Valve P is opened and adjusted for the same optimum sample pressure as above. A record is made and peak heights measured.

Calculation of Enrichment

From the peak heights measured above, ratios of the individual components to He are calculated for both the "direct" and "separator" flow conditions. Enrichment N is calculated by dividing the "separator" ratio by the "direct" ratio.

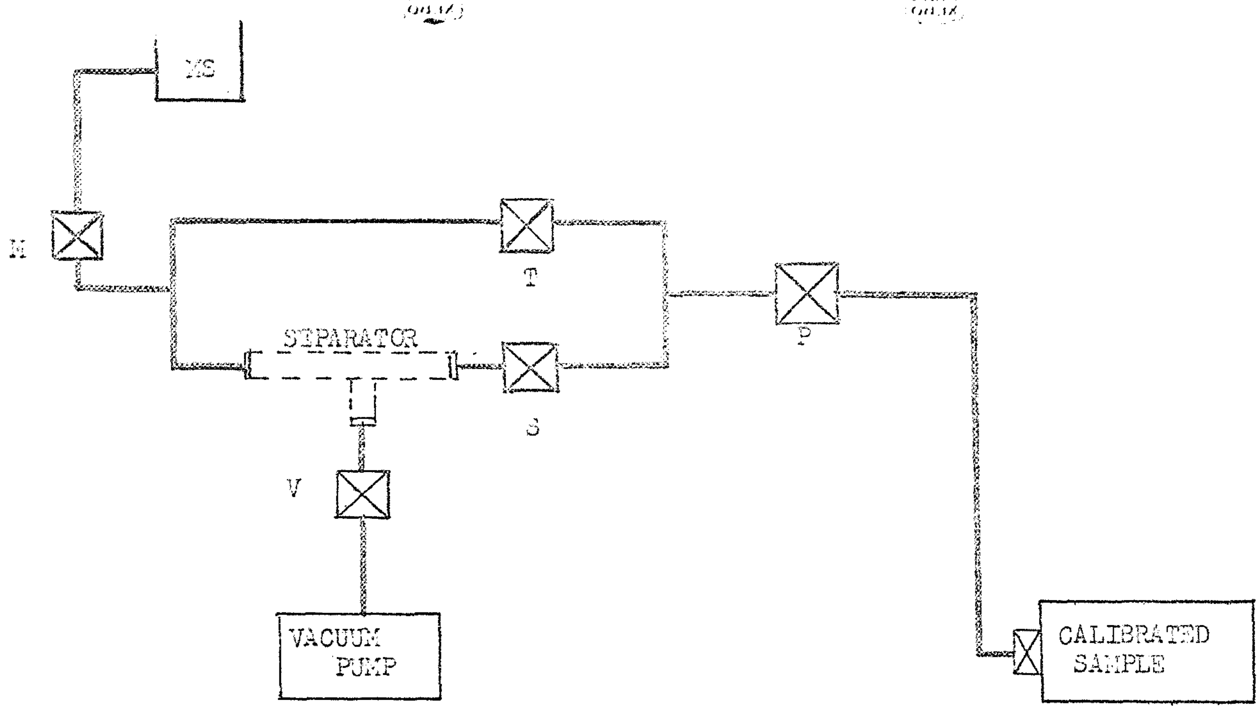

FIGURE 1 A SEPARATOR TEST SYSTEM

SYSTEM TEMPERATURE 22°C FOR ALL TESTS

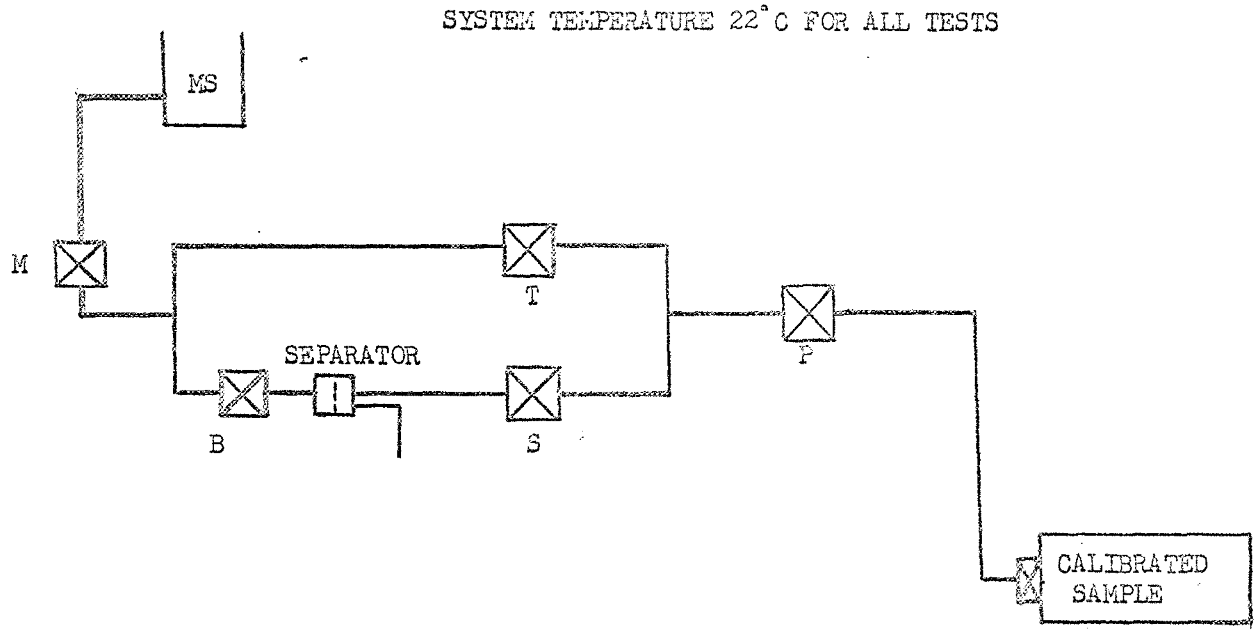

FIGURE 1 B SEPARATOR TEST SYSTEM

Separator Enrichment - Ryhage Type Separator

This quantity is calculated below:

Gas	Direct	Separator	M.W.
He	90	14	4
Ne	430	145	20
Ar	1400	600	40
Freon 14	1400	800	88
Xe	230	145	131

Ratios	Direct	Separator	N*
Ne/He	4.78	10.35	2.2
Ar/He	15.56	42.85	2.8
Freon/He	15.56	57.14	3.7
Xe/He	2.56	10.35	4.0

*Separator/Direct - Enrichment

When N is plotted vs. molecular weight, a reasonable relationship is developed between these two quantities. See Fig. 2.

B. Blummer Silver Foil Separator

This separator was built following the original design of Max Blummer, Woods Hole Oceanographic Institute.

The He hydrocarbon mix is passed thru the straight

RYHAGE TYPE SEPARATOR

ENRICHMENT (f) M.W.

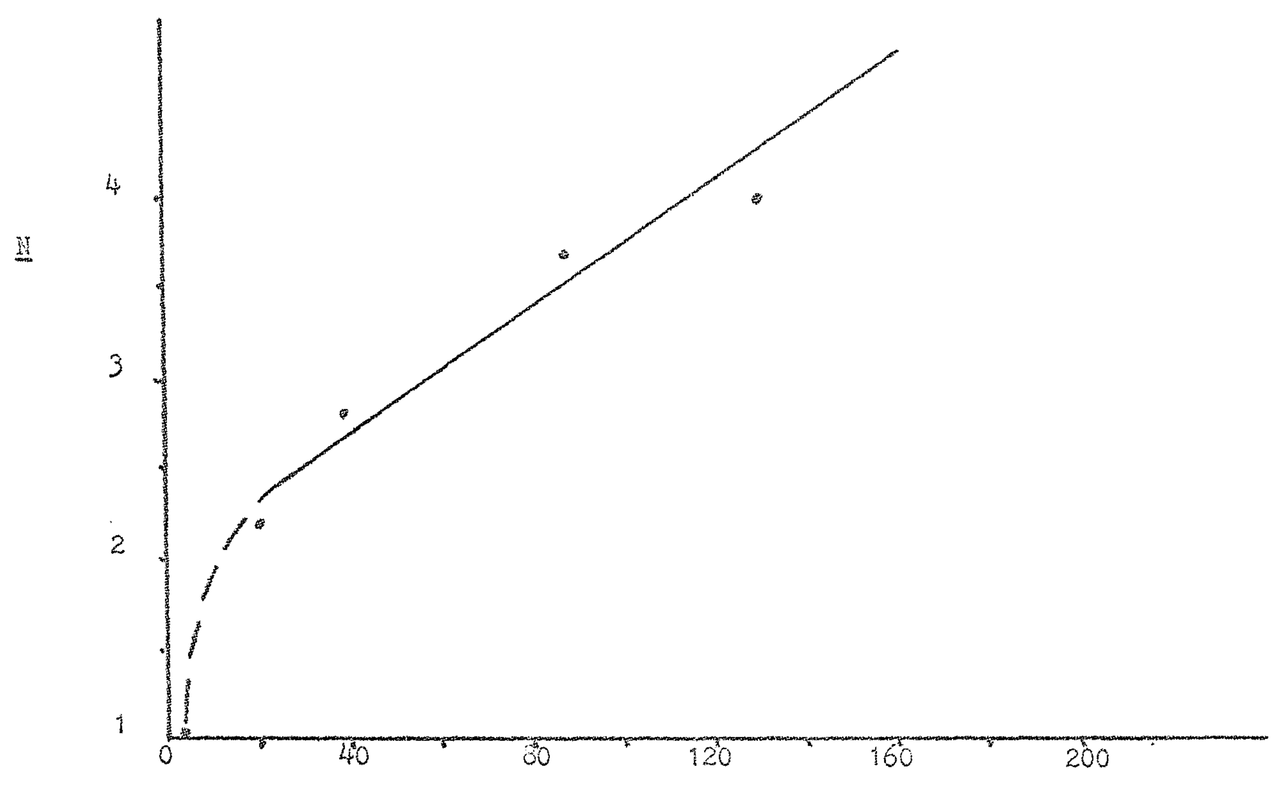

FIGURE 2

section of a 1/4" S. S. Swagelock tee, which is inserted in the "Separator" position in Fig. 1A. A 1/4" diameter piece of silver membrane filter material 2 mils thick and 3 micron maximum pore diameter, is inserted in the side arm between a 1/4" metal washer and a 1/4" OD. silicone rubber "O" ring. A piece of 1/4" tubing holds this assembly in place. The fitting is made up with teflon ferrules which hold the tubing tight against the "O" ring. A mechanical vacuum pump is connected to the tubing, pulling gas thru the silver membrane material from the He/hydrocarbon mix passing thru the straight part of the tee.

To test this separator two gas mixtures were prepared. Mix A contained 50% He, 25% CO_2, 25% $Freon_{22}$. Mix B contained 50% He, 25% $Freon_{12}$, 25% Freon C-318. The individual components of these mixtures were chosen to give a wide range of molecular weights along with minimum cross interference in the mass spectra.

The test procedure used was the same as described for the Ryhage model, passing the sample directly into the spectrometer to obtain the "direct" measurements and then thru the operating separator to obtain the "separator" measurements. These measurements are given below:

Mix A	Direct	Separator	M.W.
He	370	240	4
CO_2	1700	1800	44
Freon 22	2000	2400	86.5
Mix B			
He	100	60	4
Freon 12	640	680	120.9
Freon 318	130	150	200.00

Ratio	Direct	Separator	N.
CO_2/He	4.59	7.50	1.6
Freon 22/He	5.41	10.00	1.8
Freon 12/He	6.40	11.33	1.8
Freon 318/He	1.30	2.50	1.9

Enrichments (N) are plotted as a function of molecular weight in Fig. 3.

BLUMER

SILVER MEMBRANE SEPARATOR

ENRICHMENT (f) M.W.

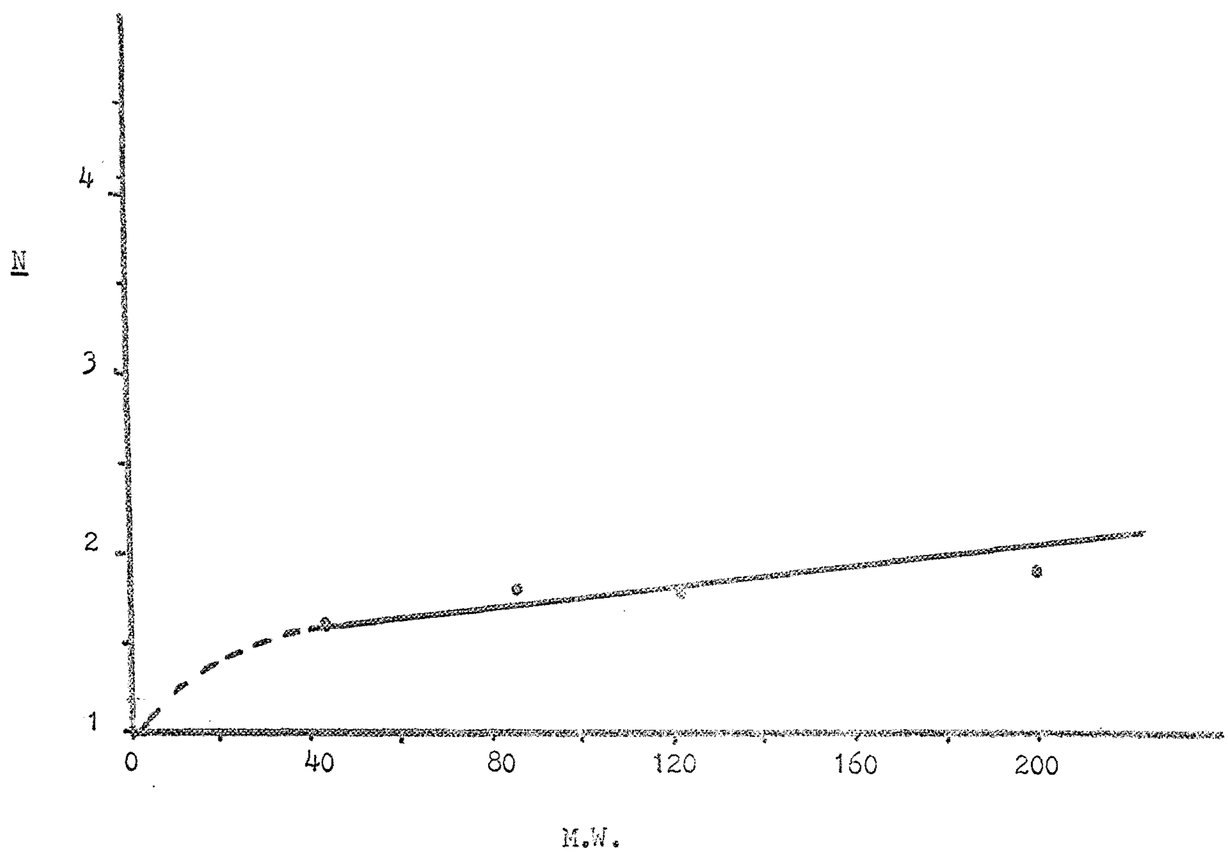

FIGURE 3.

C. Varian Molecular Separator

A Varian V-5620 Molecular Separator, working on the principle of hydrocarbon vapors dissolving in and passing thru an organic membrane, was obtained on loan from JPL. It was installed in the valved by-pass system as shown in Fig. 1B. With valve B shut, "direct" measurements are made as described under the Ryhage or Blummer separator test procedure. With valve B open, T shut and S open, sample gases are introduced thru metering valve P and "separator" measurements made as described previously.

Two membranes were supplied with the separator and, unfortunately, both had sufficiently large leaks thru the membrane to make it impossible to obtain MS pressures of less than 2x10-4. Since this pressure is too high to operate the MS, several attempts were made to find and seal the leak, but these proved to be unsuccessful. Two new membrane assemblies were finally obtained from Varian Associates and the test program started.

Mix A and Mix B, used in the Blummer separator test program, were passed thru the separator and enrichments calculated. These were in the range of 1.5 to 2.5, much lower than expected.

In a discussion of these results with Varian Associates, it was determined that the membrane temperature should be at least 15°C lower than the boiling points of the hydrocarbons to be separated. As the Freons in mixes A and B have boiling points in the range of -6°C to -41°C, cooling to -56°C would be necessary to use these materials as test mixes.

Since many of the components expected from the pyrolysis process in the GC/MS experiment would be in the higher boiling point range, a mixture of 50% 1-1-1 trichloroethane (BP-80°C-Av.) and 50% ethyl decanoate (BP 111°C) was made and He bubbled thru the liquid mixture. A distinct improvement in enrichment was observed as shown below:

Gas/Vapor	Direct	Separator	M.W.
He	550	150	4
111 Trichloro-ethane	120	250	133.4
Ethyl Decanoate	6	13	200.3

Ratio	Direct	Separator	N
111 Trichloro-ethane/He	0.22	1.7	7.6
Ethyl Decanoate/He	0.11	0.87	7.9

The presence of air peaks in the spectrum indicated a leak at the separator membrane gasket. This was corrected and a similar test run on He bubbled thru 1-1-1 trichloroethane. A further improvement in enrichment was observed:

Gas/Vapor	Direct	Separator	M.W.
He	190	20	4
111 Trichloro-ethane	90	120	133.4

Ratio	Direct	Separator	N
111 Trichloro-ethane/He	0.47	6.0	12.8

The Varian separator is, by far, the most efficient unit tested in this program. The unit as tested could be made more efficient for a given set of hydrocarbon compounds by optimizing the operating temperature. It is possible to use these membranes in a two stage configuration, pumping with a mechanical pump on the space between membranes. Enrichments, for some hydrocarbons, of over 1000, have been reported for this configuration. Difficulty might be expected in the measurement of trace quantities of fixed gases or other low boiling point materials.

Two Lipsky heated teflon tube separators were constructed, but difficulty was experienced with leaks through the teflon tubing and at the teflon - s.s. tubing connections. Tests could not be completed on these units.

Measurements were made of the efficiency of recovery for the Ryhage type unit, with the concept of sampling the peripheral volume for enhancement of the lighter gas components. It was hoped that this concept could be applied to the enhanced measurement of low molecular weight gases in a high percentage CO_2 planetary atmosphere. Efficiencies for this unit fell in the range of 1 to 2%, obviating any possibility of using this unit for this application. The fritted stainless steel separator, built by Dr. McCloskey - Baylor School of Medicine, is reported to have efficiencies in the 40 to 50% range and might be applied to this particular measurement. A physical redesign would be required since the original model was made to be part of the vacuum port of his mass spectrometer.

By masking the electron multiplier aperture of our Finnigan mass spectrometer, the helium noise background was reduced sufficiently to give an effective sensitivity increase of a factor of three. This improved sensitivity would be quite useful in both the GC/MS application and in atmosheric measurement problems. Had time permitted, additional separator tests would have been made and other sensitivity improvement concepts explored.