NAS 9-14763

NASA CR- 150942

FLIGHT CONTAMINANT TRACE ANALYSER

PHASE I: CHROMATOGRAPHIC INPUT SYSTEM

Final Report

September 1976

(NASA-CR-150942) FLIGHT CONTAMINANT TRACE ANALYSER. PHASE 1: CHROMATOGRAPHIC INPUT SYSTEM Final Report (Ionics Research, Inc., Houston, Tex.) 17 p HC $3.50 CSCL 07D

G3/25

N76-31306

Unclas

02471

IONICS RESEARCH, INC.

22 Sandalwood Drive

Houston, Texas 77024

Albert Zlatkis, President

SUMMARY

The purpose of this investigation was to develop 2 chromatographic columns which would enable a mass spectral identification of 40 specified compounds. The end-use of these columns will be as part of a toxic gas analyser, which incorporates an automated gas chromatograph-mass spectrometer. The column development work was, therefore, constrained by the use of low carrier gas flow rates of hydrogen (nominally $\leq$5 cc/min), and both sampling and interface considerations compatible with the efficient operation of the mass spectrometer.

Six different types of stationary phases have been investigated during the course of this effort. The columns used were of the open tubular capillary type and were made of nickel. Limitations of initial and final temperature of operation led to final development of a column which could resolve most of the compounds required. The few unresolved components are capable of resolution and identification by the mass spectrometer. The columns (182m Ni x 0.8m O.D x 0.5mm I.D) coated with Witconal LA 23, yielded in excess of 200,000 theoretical plates and completed the analysis in less than 90 minutes using a carrier gas flow rate of 4 cc/min hydrogen.

INTRODUCTION

1.1 Objective

The primary objective of this study is to prepare two chromatographic columns which are capable of resolving 40 given organic components present in the atmosphere of manned spacecraft (Table 1). The operational requirements include the potential use of hydrogen as a carrier gas with a maximum flow rate of 5 ml/min.

MATERIALS AND METHODS

2.1 Analytical equipment

Evaluation of column performance was made on a Perkin Elmer Model 3920 gas chromatograph using a Shimadzu 1 mv potentrometric recorder.

2.2 Carrier gas

After initially using helium as the carrier gas it was decided to change to hydrogen for the following reasons:

(a) gas chromatograph-mass spectrometer being designed by Beckman/Perkin-Elmer will be using a Palladium separator. This requires the use of hydrogen as a carrier gas.

(b) the time for analyses would be significantly reduced without a corresponding loss in resolution.

2.3 Test samples

Table 1 is a list of the 40 chemical compounds that have been identified as present in spacecraft atmospheres. Each of the compounds has been assigned a number for identification purposes. Since liquid samples were used to evaluate the columns, a 34 component mixture was prepared as the test mixture.

2.4 Columns

The initial study (see Final Report NAS 9-14001) concluded that open tubular capillary columns would be the most desirable. Since nickel tubing has better thermal characteristics and is easily coated (1) the high degree of resolution required obviated the use of packed columns or short support coated open tubular columns. Further, previous studies have indicated that the use of hydrogen as a carrier gas in nickel columns posed no problems (1). Columns were, therefore, obtained from Handy and Harman Tube Company, Norristown, Pennsylvania in lengths of 91.4m, O.D. = 0.8mm, I.D. = 0.5mm.

The compounds listed in Table 2 were used as stationary phases in an attempt to effect better resolution, and minimum analysis time. All of these phases are moderately polar and have comparable temperature limitations of 170°C. In each case a 91.4m column was coated and tested.

2.5 Conditioning of columns

In order to minimize bleed from chromatographic columns it is

TABLE 1.

Numbering System for Spacecraft Organics

Boiling Point °C	Compound	Code number
-191.5	Carbon monoxide	1
-24.2	Methyl chloride	2
-6.3	1-Butene	3
-4.4	1,3-Butadiene	4
9.0	Dichlorofluoromethane	5
20.8	Acetaldehyde	6
34.0	Isoprene	7
37.0	Vinylidene chloride	8
40.0	Methylene chloride	9
48.8	Propionaldehyde	10
53.0	Acrolein	11
65.0	Methanol	12
67.0	Tetrahydrofuran	13
74.1	Methylchloroform	14
75.7	Butyraldehyde	15
76.5	Carbon tetrachloride	16
77.0	Ethyl acetate	17
79.6	Methyl ethyl ketone	18
80.1	Benzene	19
82.4	Isopropanol	20
83.4	1,2-Dichloroethane	21
87.0	Trichloroethylene	22
97.4	n-Propanol	23
99.5	Isobutanol	24
101.0	1,4-Dioxane	25
101.6	n-Propyl acetate	26
110.6	Toluene	27
117.2	Isobutyl acetate	28
117.2	n-Butanol	29
118.0	Methyl isobutyl ketone	30
121.0	Tetrachloroethylene	31
126.5	Butyl acetate	32
132.0	Chlorobenzene	33
136.2	Ethylbenzene	34
138.4	p-Xylene	35
139.1	m-Xylene	36
145.2	Styrene	37
159.2	n-Propylbenzene	38
164.7	Mesitylene	39
180.5	o-Dichlorobenzene	40

TABLE 2.

STATIONARY PHASES TESTED

(1) Neopentyl glycol succinate

(2) UCON 50 HB 2000

(3) UCON LB 1200 X

(4) TRITON X-305

(5) Emulphor ON-870

(6) Witconal L-23*

*Witconal LA-23 is a polyoxyethylene lauryl ether which is normally used as an oil-in-water emulsifier. It is available from Witco Chemical Corporation, 3230 Brookfoeld, Houston, Texas 77045.

the usual practice to condition or stabilize the column with carrier gas flowing, at an elevated temperature, generally at least 20°C above the maximum operating temperature. It was necessary, therefore, to condition all capillary columns prior to use. The procedure was standarized as follows: with the carrier gas flow rate set to between 5 and 10 cc/min, the column was first heated for one hour at 50°C, and the temperature then raised by programming at 2°/min to a temperature 20°C above the highest temperature at which the column was to be operated. For example, for the Witconal phase a maximum column temperature of 150°C was selected, therefore, the conditioning temperature was set to 170°C. The column is then held at this final temperature for eight hours.

However, it is important to recognize that each liquid phase also has its own maximum temperature of operation, which depends, of course, on its thermal stability. In the case of the Witconal phase this temperature is approximately 170°C, consequently, columns coated with Witconal were always operated at a temperature considerably below this value to ensure minimal bleed.

2.6 Selection of the liquid phase

During the course of this study it became apparent from limitations imposed by the GC/MS system that the column would have an initial temperature of 60° and then be programmed to 120° whereas all of the stationary phases tested could meet these particular requirements the resulting resolution was unsatisfactory for most of them - particularly for the lower molecular weight compounds.

RESULTS

3.1 Performance of open tubular columns

Six stationary phases were tested on 91.4m x 0.5mm I.D. nickel open tubular columns. None of these columns fulfilled all of the requirements of the Flight Contaminant Trace Analyzer. Evaluations were made on the basis of separating alcohols, aromatics and a test mixture containing most of the desired components. The unsuccessful columns and reasons for their preliminary rejection are listed in Table 3.

The requirements of an initial temperature of 60° made resolution of early components very difficult. Although Column 6 (Witconal LA-23) appeared best for the overall separation, it too could not resolve the low molecular weight compounds. A compromise was reached by using a column of twice the length, i.e. 182m. This column could indeed resolve compounds 6 through 40 except for tetrahydrofuran, methylchloroform and butyraldehyde which appear as one peak. These and peaks 1-5 are easily identifiable by mass spectrometry.

A chromatogram of the final column is shown in Figure . The operating conditions were as follows:

184m x 0.5mm I.D. Nickel Witconal LA-23 column
Carrier gas: hydrogen
Flow rate: 4 ml/min
Temperature: 60° isothermal for 30 minutes
40/min to 120°
isothermal at 120°
Time of analysis: 85 minutes

TABLE 3.

CAPILLARY COLUMN PERFORMANCE

Column = 91.4m x 0.5mm I.D.	Comments
(1) Neopentyl glycol succinate	alcohols not resolved - some tailing difficulty in coating column
(2) UCON 50 HB 2000	methanol tails - 25 compounds resolved
(3) UCON LB 1200 X	methanol tails - 23 compounds resolved
(4) TRITON X-305	aromatics and halocarbons poorly resolved
(5) Emulphor ON-870	24 of 34 compounds resolved under the desired conditions

4.0 Column preparation

Two columns were coated with Witconal LA-23 phase in preparation for final column testing. The procedure for coating the 184m by 0.5mm I.D. columns was standardized as follows:

Coating Solution:

10.0 grams of Witconal LA-23
Dissolve in 100ml of chloroform

A 20ml aliquot of this coating solution was added to a reservoir to which the cleaned capillary column was attached. A source of nitrogen gas was connected through a Brooks flow controller to the reservoir with the outlet pressure set to 12psi. The velocity of the coating solution through the column was adjusted by means of the flow controller to 3 mm/sec. The carrier gas flow was maintained for a minimum of two hours to remove excess solvent. The column was then conditioned as described in Section 2.5. Columns were tested with an injection of alcohols and m- and p- aromatics. Satisfactory resolution of m- and p- xylene and the lack of tailing of C_{1-4} alcohols was taken as the first indication that the column was acceptable. To confirm performance the multi-component mixture was injected.

5.0 Interface with the Mass Spectrometer

The principal consideration associated with the integration of any chromatographic column with a mass spectrometer is the maximum permissible carrier gas flow rate. For the purposes of the column development work the [illegible] flow rate was set not to exceed 5 cc/min.

Only hydrogen as a carrier gas has been used in the present experiments. Hydrogen was necessary since it must be used with the Palladium/Silver separator. The Viking/Mars Gas chromatograph-Mass spectrometer is, in fact, interfaced with an electrochemical Palladium/Silver separator and has already been subjected to the rigors of flight acceptance tests.

Also of importance in GC-MS applications is the extent of column bleed. There are two aspects to this question, first column bleed must not be so great so as to cause an increase in the ion source pressure, and secondly it should not contribute so many fragment ions that they interfere with the mass spectral interpretation. The Witconal phase has, of course, been selected for its separation characteristics with respect to the resolution of the 40-component test mixture. There is, however, some concern that their polar structure could contribute to long term poor thermal stability. To offset this potential problem, a maximum operating temperature of 120°C has been set for the Witconal column, and this is reached during temperature programming rather than set isothermally.

6.0 Column Testing

Column testing was effected using the experimental arrangement illustrated in Figure 2. 1 ml vapor samples of the test mixture are injected every hour by an automatic sample injection valve (Valco Instrument Co., Houston, Texas), driven by an air operated solenoid. The actual sample valve configuration is shown in Figure 3. The column was run for a period of 60 days and checked chromatographically on alternate days.

7.0 Column Delivery

Columns were delivered to the Accountable Property Officer 807402 (received by Wayland J. Rippstein) as follows:

February 19, 1976 Column No. AZ-1 NAS 9-14763

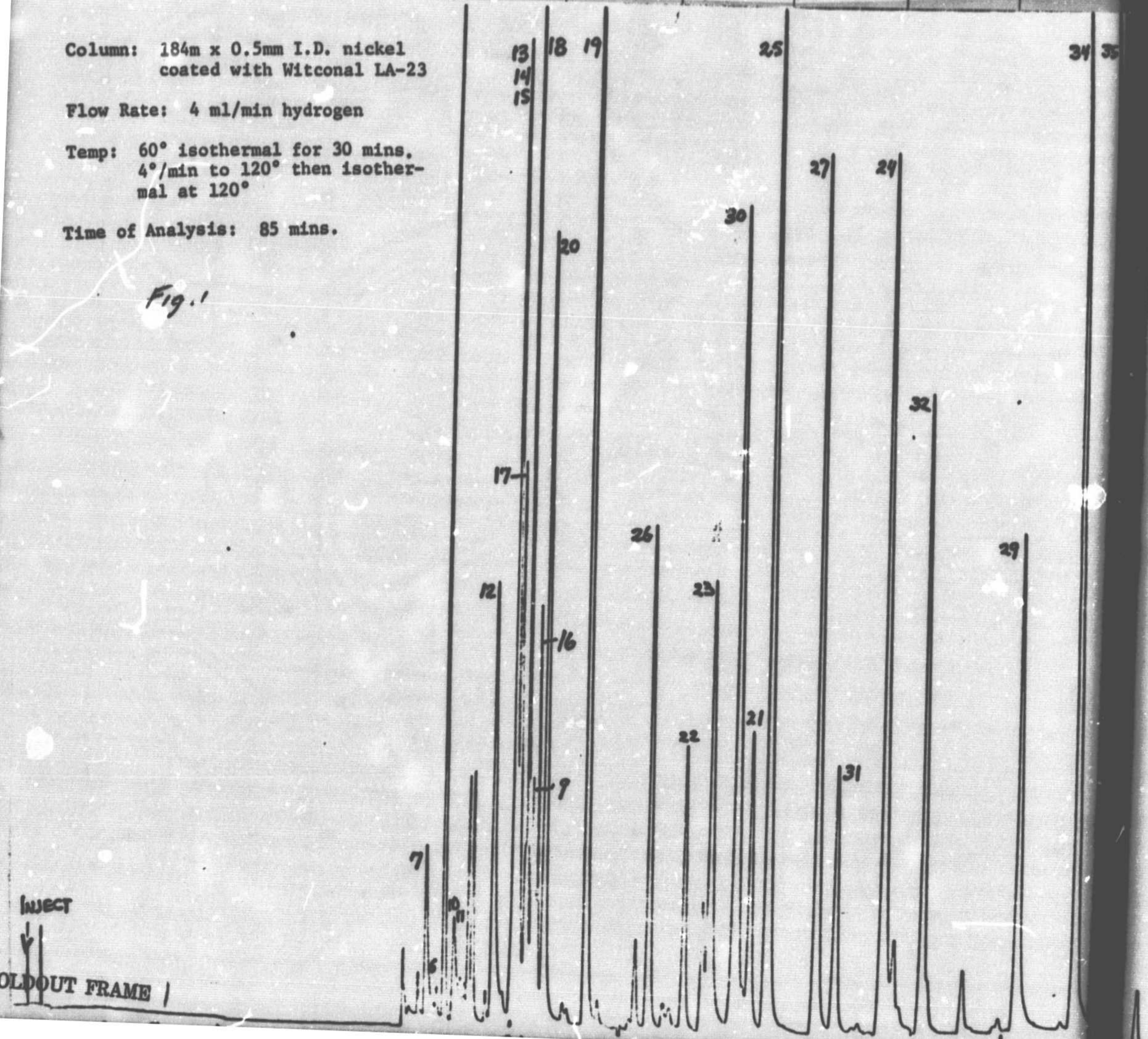
July 29, 1976 Column No. AZ-2 NAS 9-14763

8.0 New Technology

During the course of this investigation, each phase of the work has been assessed for any developments which might possibly be regarded as new technology. All of the methods used in preparing and testing columns are considered to be state-of-the-art. No novel or original items of hardware or recipes have been developed as a consequence of this work; and we believe, therefore, that there are no areas of this research which would qualify as items of new technology.

REFERENCES

(1) W. Bertsch, F. Shunbo, R. C. Chang and A. Zlatkis, Chromatographia, 7, 128 (1974).



Column: 184m x 0.5mm I.D. nickel coated with Witconal LA-23

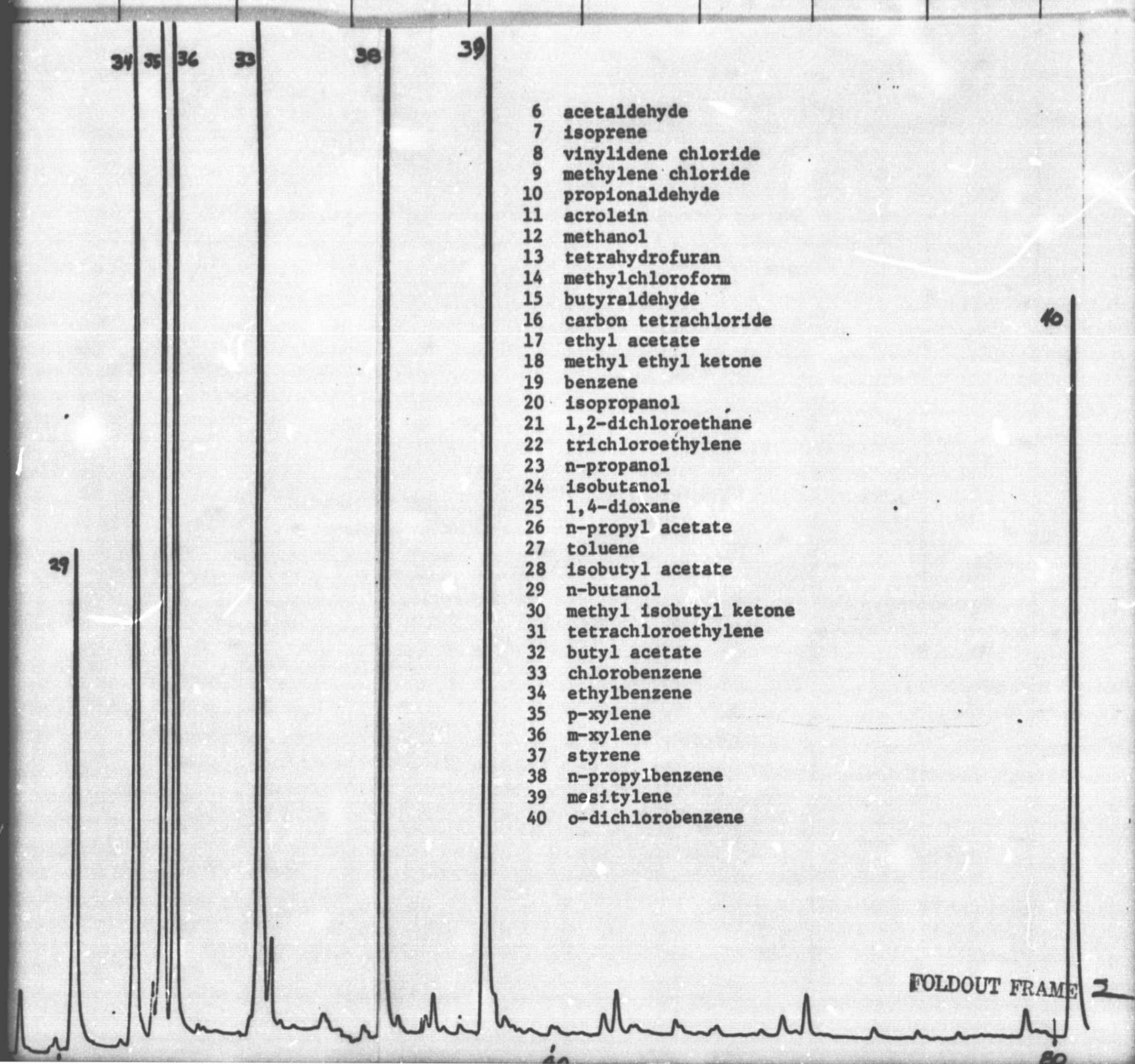
Flow Rate: 4 ml/min hydrogen

Temp: 60° isothermal for 30 mins, 4°/min to 120° then isothermal at 120°

Time of Analysis: 85 mins.

Fig. 1

OLDOUT FRAME 1



6	acetaldehyde
7	isoprene
8	vinylidene chloride
9	methylene chloride
10	propionaldehyde
11	acrolein
12	methanol
13	tetrahydrofuran
14	methylchloroform
15	butyraldehyde
16	carbon tetrachloride
17	ethyl acetate
18	methyl ethyl ketone
19	benzene
20	isopropanol
21	1,2-dichloroethane
22	trichloroethylene
23	n-propanol
24	isobutanol
25	1,4-dioxane
26	n-propyl acetate
27	toluene
28	isobutyl acetate
29	n-butanol
30	methyl isobutyl ketone
31	tetrachloroethylene
32	butyl acetate
33	chlorobenzene
34	ethylbenzene
35	p-xylene
36	m-xylene
37	styrene
38	n-propylbenzene
39	mesitylene
40	o-dichlorobenzene

FOLDOUT FRAME 2

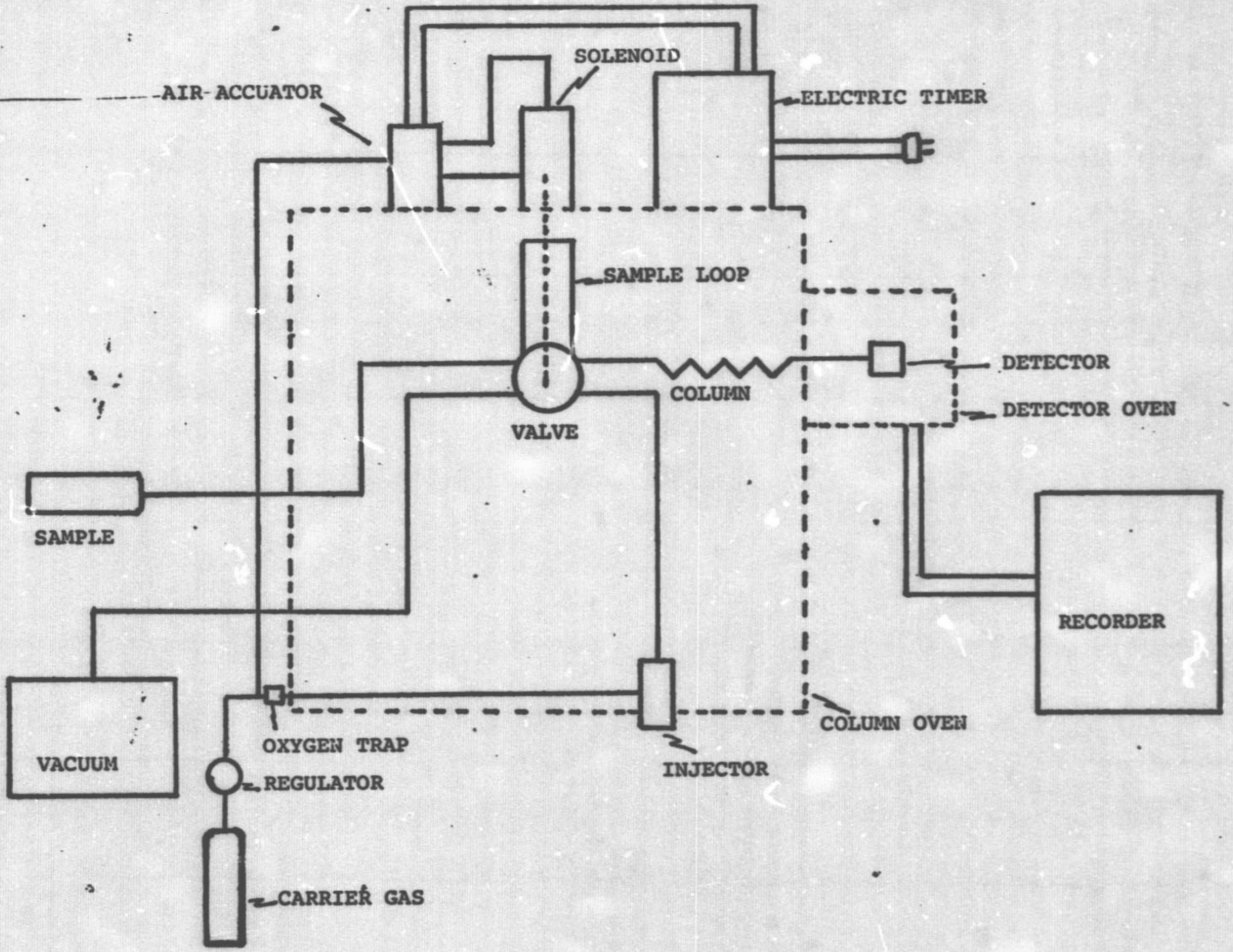
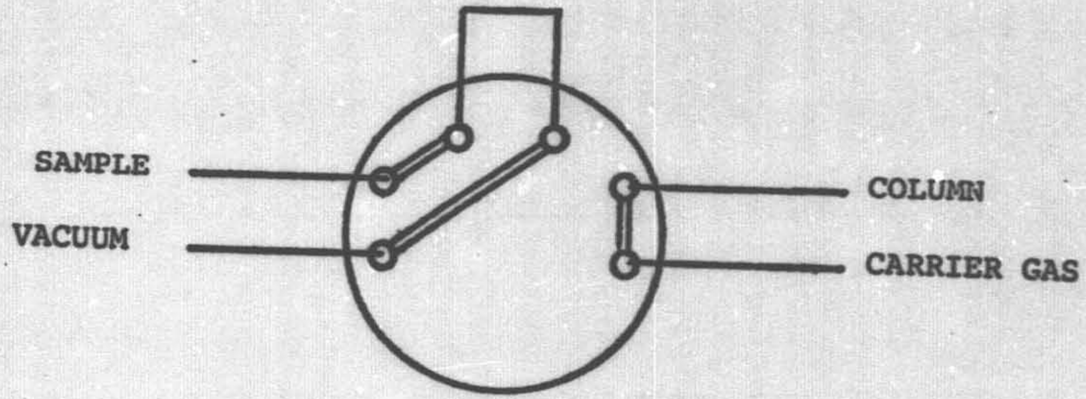
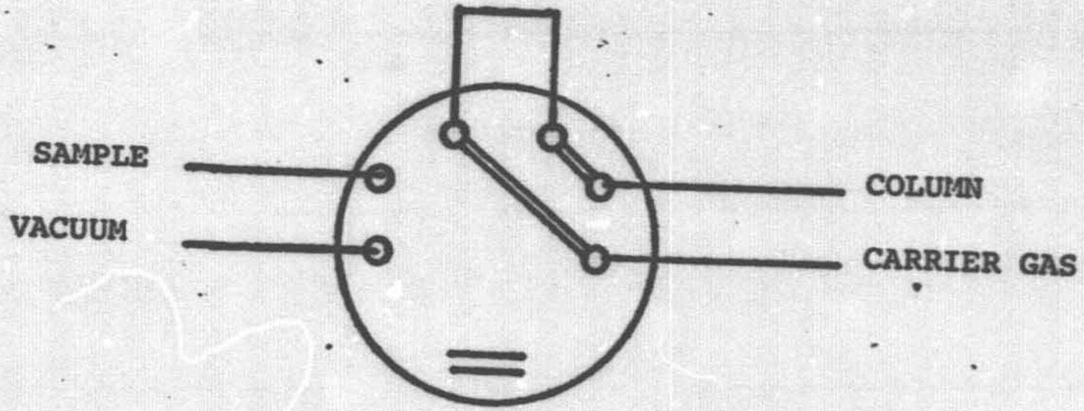


FIGURE 2.
SAMPLE TEST SYSTEM



SAMPLE



INJECT/ANALYZE

SAMPLE VALVE CONFIGURATION

FIGURE 3.