NAS 9-14001

NASA CR-
141733

FLIGHT CONTAMINANT TRACE ANALYSER

PHASE I: CHROMATOGRAPHIC INPUT SYSTEM

Final Report

April 1975

(NASA-CR-141733) FLIGHT CONTAMINANT TRACE ANALYSER. PHASE 1: CHROMATOGRAPHIC INPUT SYSTEM Final Report (Ionics Research, Inc., Houston, Tex.) CSCL 14B
N75-21588
Unclas
G3/35 18609

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SUMMARY

The purpose of this investigation is to develop a chromatographic column which is capable of resolving forty compounds, associated with the atmospheres of spacecraft. The end-use of this column will be as part of a toxic gas analyser, which incorporates an automated gas chromatograph-mass spectrometer. The column development work is therefore constrained by the use of low carrier gas flow rates, (nominally $<$ 10 cc/min), and both sampling and interface considerations compatible with the efficient operation of the mass spectrometer.

Three different types of column have been investigated during the course of this effort, small diameter packed columns, support coated open tubular columns, and open tubular or capillary columns. The packed columns are the easiest to prepare and operate in practice, but do not have enough efficiency to resolve more than about half of the compounds in the test mixture. The support coated open tubular, (S.C.O.T.) columns are obtained commercially from the Perkin Elmer corporation and have excellent efficiency, and large sample capacity. However, in general, they gave unsatisfactory performance with polar compounds, such as methanol, producing unsymmetrical peaks with pronounced tails. The only S.C.O.T. column which gave symmetrical peaks for alcohols was coated with Carbowax 20M. But unfortunately this

column did not have adequate resolving power for the test mixture, since approximately 25% of the test compounds remained unseparated. Capillary columns appear to be the most attractive for solving the objectives, and have been coated with phases which give acceptable peak symmetry for different compound types with varying degrees of polarity. Based on a substantial amount of testing a 91.4 meter by 0.05 cm i.d capillary column coated with a mixture of Polyalkylene glycols (Ucon 50HB2000 + Ucon LB1200X) has been found to provide the best selectivity for resolving multicomponent mixtures of the type found in spacecraft atmospheres. Both temperature programming and isothermal operation of the column have been evaluated, and it is believed that temperature programming offers distinct advantages; with a much shorter total analysis time for a given carrier gas flow rate, and overall superior resolution. It has also been observed that an approximately 15% saving in analysis time can be acheived with hydrogen as the carrier gas compared to helium. Analysis of the 40-component test mixture is completed within 45 minutes provided temperature programming is used and 38 of the 40 test compounds are well resolved. Two pairs of compounds, methyl chloride and 1,3-butadiene, and also methylene chloride and ethyl acetate cannot be separated on the mixed phase Ucon column, while toluene and tetrachloroethylene are only 50% resolved. Nevertheless, for all practical purposes all of the other components in the mixture are 100% resolved.

Following the optimisation of the column operational parameters, a mixed, phase Ucon capillary containing 90% Ucon 50HB2000 + Ucon LB 1200X has been prepared for evaluation during the column test period in which the test sample is automatically analysed once every hour over a thirty-day test period. Column efficiency will be checked on a regular basis to ensure that there is no deterioration of column performance. Consideration has also been given in this study to sampling techniques and a maximum sampling volume of 1ml has been determined experimentally for the candidate Ucon column. Attention has also been paid to the problem of interfacing the column with a mass spectrometer, and a maximum operating temperature of 120°C has been placed on the column as an operational constraint, to minimise column bleed. Compounds which are unresolved are also discussed in relation to their possible effect on the interpretation of mass spectral data.

1. INTRODUCTION

1.1 Objectives

The primary objective of this study is to develop a chromatographic column, or columns, and the experimental conditions necessary to separate forty organic compounds present in the atmosphere of manned spacecraft.

In addition, consideration is given to sampling, column parameters, and operation and column interface with a mass spectrometer.

2. MATERIALS AND METHODS

2.1 Analytical equipment used in investigation

The assessment of column performance was carried out using a Model 5700A Hewlett Packard gas chromatograph equipped with its own potentiometric recorder (Model 7123A). The chromatograph was used without modification, however, due to the low flow rate of carrier gas through the columns, an auxillary flow of nitrogen gas was added to the carrier flow prior to entering the detector to maintain optimum flame ionization sensitivity.

2.2 Carrier gas

Helium was used as the primary carrier gas and the flow rate for all columns tested was maintained at less than 10cc/min. Some experiments were also performed with hydrogen as the carrier gas, since it is well known that the overall analysis time may be significantly reduced when using hydrogen without a drastic reduction in column resolution.

2.3 Preparation of test samples

Table 1 is a list of the forty chemical compounds that have been identified as present in spacecraft atmospheres. Each of the compounds has been assigned a number for identification which corresponds with the numbering system used in the statement of work, except that the ten display compounds are numbered 1A through 10A.

TABLE 1.

Numbering System for Spacecraft Organics

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

[*] Used as equivalent gas chromatographic substitute for detection by flame ionization.

Initially samples were prepared in methanol solution for each class of compound, (e.g. aromatics, halocarbons, etc.) However, later samples were prepared as mixtures of the pure compounds, without solvent. These were prepared by adding each of the compounds to a 30ml sample vial in roughly inverse proportion to their vapour pressures . This ensures that approximately equal proportions of each component will be acquired when a vapor sample of the head space is taken from the mixture. The sample vial is sealed with a serum cap, and components which are gases at S.T.P, were then added to the mixture by injection through the serum cap with a gas syringe. Vapor samples of the mixture head space were acquired with the same 10ml gas syringe, although 1cc of vapor or less was generally injected into the chromatograph.

Methane has been substituted for carbon monoxide in the test mixture, since the latter does not respond in the flame ionization detector. This is a justifiable substitution on a chromatographic basis as neither gas is apprecia bly retained by the majority of columns.

2.4 Column types

Since any candidate column is to be eventually mated with a mass spectrometer this automatically restricts the type of column which can be used to one with a flow rate compatible with the GC-MS interface and the pumping capacity of the mass spectrometer. As an operational requirement this flow rate was not to exceed 10cc/min (STP). There are three possible column types which are well suited to these low flow rates, and also have adequate efficiency for the resolution of multicomponent mixtures.

A. Small diameter packed columns (S.D.P.)
B. Support coated open tubular columns (S.C.O.T.)
C. Open tubular or capillary columns (O.T.)

All three types have been tested during the course of this investigation.

2.4.1 Small diameter packed columns

All of the packed columns investigated in this study were prepared from type 321 seamless stainless steel tubing with an outside diameter of 0.159cm. The majority of columns had an internal diameter of 0.127cm, although a few columns were prepared from tubing with a smaller internal diameter. (Either 0.1 or 0.076 cm) Chromatographic packings were obtained either commercially, or prepared by coating various stationary phases onto inert supports, by the filtration technique.

Three distinct types of packing material have been used to prepare the columns.

A. Conventional inert supports, such as the diatomaceous earths, (Gas Chrom Q, etc;) coated with different stationary phases.

B. Chromatographic packings with chemically-bonded liquid phases.

"Durapak"

(Waters Associates, Framington, Mass.)

C. Porous polymers

Poropak, a styrene-divinylbenzene copolymer.

Tenax, a polymer of 2, 6-diphenyl-p-phenylene oxide

Table 2 lists the various packed columns which have been tested and their configeration.

2.4.2 Support coated open tubular columns (S.C.O.T.)

S.C.O.T. columns were obtained commercially from Perkin Elmer Corporation All of the columns had an internal diameter of 0.05 cm and were coated with liquid phases of varying polarity. Columns, as supplied, are nominally 15.25 meters in length. Longer columns were obtained by coupling together individual columns with Swagelock low-dead volume unions. The different types of S.C.O.T. columns which have been investigated are listed in Table 3.

2.4.3 Open tubular or capillary columns.

Capillary columns were prepared from type 316 stainless steel tubing obtained from the Perkin Elmer corporation in 91.4 meter lengths. All of the Perkin Elmer columns had an internal diameter of 0.05 cm. 0.076 cm i.d stainless steel tubing was acquired from Handy and Harmon Tube company (Norristown, Pennsylvannia. " Chromat I.D. grade 316 stainless). The different types of capillary column which have been tested are reported in Table 4.

TABLE 2.

		Column dimensions			Column packing	
		Length (m)	I.D. (cm)	% loading	Phase	Support
A.	1.	3.0	0.127	10	OV101 silicone	80-100 mesh Gas Chrom Q
	2.	3.0	"	5	Polymetaphenoxylene	" " "
	3.	3.0	"	10	Ucon 50HB2000	" " "
	4.	3.0	"	10	Didecyl phthalate	80-100 mesh Chromosorb 750
	5.	3.0	"	10	Pennwalt 223 + 4% KOH	80-100 mesh Gas Chrom R
	6.	3.5	"	10	Neopentylglycol isophthalate	80-100 mesh Gas Chrom Q
	7.	3.5	"	12	Stabilised Diethylene glycol succinate	90-100 mesh Anakrom ABS
	8.	4.0	"	5	Diisodecyl phthalate + 1% Bentone 34	80-100 mesh Gas Chrom Q
	9.	4.0	"	10	Silar 10C	80-100 mesh Anakrom Q
B.	10.	2.74	0.127		Durapak (Low K) Carbowax 400/Porasil F.	100-120 mesh
	11.	4.3	"		" " " "	" "
	12.	3.0	"		Mixture Durapak (Low K) + Carbowax 400/Porasil C	" "
	13.	3.0	"		Mixture Durapak (Low K) + Chromosorb 101.	" "
C.	14.	2.0	0.076	2	Polymetaphenoxylene	60-80 mesh Tenax-GC
	15.	2.0	0.127		Poropak Q	80-100 mesh
	16.	3.0	"	2	OV101 silicone	80-100 mesh Poropak Q

TABLE 3.

Types of Support Coated Open Tubular Columns Investigated.

Column length (m)	Liquid phase
15.25 30.5 45.75	MBMA. Metabismeta-phenoxyphenoxybenzene + Apiezon L.
30.5	OV 1 (Methyl silicone)
30.5	OV 17 (Methyl phenyl silicone)
30.5	Silar 10C (Cyanopropyl silicone)
15.25 30.5	Carbowax 20M
30.5 45.75 61.0	Ucon LB550X
Combination columns:	
30.5	Ucon LB550X (15.25m) + Carbowax 20M (15.25m)
30.5	Ucon LB550X " + MBMA "
30.5	Carbowax 20M " + Ucon LB550X "
30.5	MBMA " + Ucon LB550X "
45.75	MBMA (30.5m) + Ucon LB550X (15.25m)

TABLE 4.

Types of capillary columns investigated.

	Column dimensions		Liquid phase	
	Length (m).	I.D. (cm).		
C.1	91.4	0.05	Ucon 50 HB2000.	
C.2	"	"	Ucon 50 HB5100.	
C.3	"	"	Ucon LB 280X.	
C.4	"	"	Ucon LB 550X.	
C.5	"	"	Ucon 50HB2000 + Ucon LB1200X	(7:3).
C.6	"	"	" "	(8.5:1.5).
C.7	"	"	" "	(9.1).
C.8	182.8	"	" "	(9.1).
C.9	91.4	"	Ucon 50HB2000 + DEGS	(9.1).
C.10	"	"	Ucon 50HB2000 + PPE*	(9.1).
C.11	"	"	Carbowax 20M.	
C.12	"	"	Polymetaphenoxylene (PMP).	
C.13	"	"	AN 600 silicone.	
C.14	"	"	OV 275.	
C.15	30.5	0.076	Diethylene glycol succinate (DEGS).	
C.16	"	"	Ucon 50HB2000.	
C.17	"	"	Ucon LB1200X.	
C.18	"	"	Dinonyl phthalate.	
C.19	"	"	Triton X-305.	

* Polyphenylether 6 ring.

2.5 Conditioning of columns

In order to minimise bleed from chromatographic columns it is the usual practice to condition or stabilise the column with carrier gas flowing, at an elevated temperature, generally at least 20°C above the maximum operating temperature. The S.C.O.T. columns, as supplied by Perkin Elmer, were already stabilised and therefore were used without further treatment. It was necessary, however, to condition all new packed, and capillary columns prior to use. The proceedure was standardised 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 Ucon phases a maximum column temperature of 120°C was selected, therefore, the conditioning temperature was set to 140°C. The column is then held at this final temperature for eight hours.

However, it is important to recognise 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 Ucon phases this temperature is approximately 200°C, consequently, columns coated with Ucon were always operated at a temperature considerably below this value to ensure minimal bleed.

2.6 Selection of liquid phases

The selection of a particular liquid phase from the several hundred which are available commercially has been limited in this investigation by a number of practical considerations.

A. The column must eventually be integrated with a mass spectrometer, and hence ideally column bleed should be minimal. This eliminates many liquid phases which have maximum operating temperatures of less than about 200°C.

B. The different classes of compounds listed in Table 1, cover a wide range of polarities, from very polar compounds such as methanol, and acetaldehyde, to relatively non-polar types such as carbon monoxide, carbon tetrachloride, and benzene. To ensure that the most polar components of the mixture are chromatographed without tailing usually necessitates the use of polar stationary phases. Unfortunately, polar phases are, in general, less thermally stable than their non-polar counterparts.

C. Candidate liquid phases should have sufficient selectivity to resolve any isomers present in the mixture, and particularly the relatively difficult meta, para-xylene separation. In addition, peak symmetry should be maintained for all compounds in the mixture regardless of their polarity.

D. Since the boiling points of the compounds in Table 1 range from -191.5 to 180.5°C, a phase which is a liquid at or near ambient temperature is also desirable, to produce adequate resolution of the lower boiling components of the mixture.

These constraints dramatically reduce the number of potentially useful phases. This number is further restricted from a cumulative knowledge of the gas chromatographic retention behavoir of organic compounds reported as, Kovats Retention Indices, Rohrschneider, and McReynolds Constants. This information does allow a modest prediction of those phases which are likely to be successful in resolving the 40-component mixture of interest. Naturally, retention characteristics for all forty compounds are not published for every possible liquid phase, especially the newer phases, and in these cases columns have been prepared and tested for their potential suitability.

3. RESULTS

3.1 Packed column performance

The packed columns listed in Table 2 under group A represent the first group of phases selected for preliminary testing. In order to obtain a rapid assessment of the potential of these phases for the resolutions required, standard mixtures for each class of the test compounds were injected into each of the candidate columns. A problem common to most of these columns was the peak asymmetry observed for polar compounds, especially methanol. All of the columns in group A, with the exception of columns 3 and 5 caused tailing of the methanol peak. This was most severe for columns coated with the non-polar phases, such as the OV101 silicone (column 1). Only one of the columns (Number 8) resolved m, and p-xylene and this was as expected due to the addition of 1%

Bentone 34, a phase specifically recommended for this purpose. Column 2, coated with Polymetaphenoxylene, was selected for testing since it is a high temperature phase with known low bleed characteristics. Unfortunately, the column was not very efficient unless operated above 100°C where the phase becomes sufficiently liquid for partitioning to occur. When a mixture of all forty compounds, listed in Table 1, was injected into each of the columns only three resolved more than half the mixture. (Columns 3, 4 and 7). Column 3 coated with the Polyalkylene glycol, Ucon 50HB2000, was the most promising both in terms of its ability to resolve isomers, including a partial separation of m, and p-xylene; and the overall peak symmetry for compounds with different functional groups. Columns 4 and 7 coated respectively with Didecyl phthalate, and Diethylene glycol succinate were less satisfactory with some tailing of the methanol peak and poor resolution of the aromatics.

An alternative approach to the problem of peak asymmetry for polar compounds is the use of a chromatographic support to which the stationary phase is chemically bonded. The " Durapak " series of packings are one such material. (Trade mark of Waters Associates, Framingham, Mass.) Columns prepared with this packing are listed under group B in Table 2. Testing of these columns revealed that the peak symmetry for compounds with different polar functionalities was generally quite satisfactory. The resolution of the 40-component vapor mixture for a 2.74 meter long column of Durapak Low K is shown in Figure 1. Increasing the column length to 4.3 meters slightly improves the resolution as shown in Figure 2, (Column 11). It is interesting to note that o-Dichlorobenzene the last compound in the mixture to be eluted fron the Durapak Low K column, occurs in less than 30 minutes and at a temperature of only 100°C. However, a helium flow rate of 9 cc/min was required to obtain reasonable resolution and peak shape. This high flow rate rules out the possible use of longer Durapak columns as an approach to further improving resolution.

Two other attempts were made to improve performance of the Durapak columns. Approximately, 5% of other packings both with longer retention characteristics were mixed wuth the Durapak Low K. Column 12 was a mixture containing another Durapak, Carbowax 400/Porasil C; while column 13 contained about 5% of the porous polymer Chromosorb 101. (Johns Manville Corporation). Although in both cases resolution was improved for the more volatile components of the mixture, the retention times for high boiling compounds, such as mesitylene and o-dichlorobenzene were increased to such an extent as to make the column analysis time impractical.

Bearing in mind that columns be interfaced ultimately with a mass spectrometer, it was considered appropriate to test a column material which is currently included as flight hardware for the Mars/Viking gas chromatograph-mass spectrometer. This material, "Tenax-GC" (a polymer of 2,6-diphenyl para-phenylene oxide) is coated with 2% Polymetaphenoxylene and has been found to be an excellent, general purpose, ultra low bleed, column for the separation of compounds with polar functionalities. Figure 3 confirms the satisfactory performance of this column for the different polarity types in the spacecraft mixture, however, only about half of the forty test compounds could be resolved with the relatively short 2.0 meter column. Unfortunately, there is some interaction between the column packing and some of the halocarbons in the mixture; e.g. carbon tetrachloride chromatographs as a broad peak. Because of this halogen interaction it was decided not to continue experiments with the Tenax column. However, if the polychlorinated solvents were found not to be of major importance in spacecraft atmospheres it would be worthwhile continuing work with the Tenax packing, since it has already undergone extensive testing as a flight column for a GC-MS application.

Poropak Q, another porous polymer based on styrene/divinylbenzene was also subjected to preliminary screening as a candidate material. (Columns 14, and 15, Group C). Although both resolution and peak symmetry were promising for this material the column had to be heated in excess of 200°C in order to elute the aromatic components of the mixture. Coating the Poropak with 2% OV101 silicone in an attempt to reduce the analysis time was not entirely successful, and since resolution also deteriorated further work on the Poropak columns was abandonded.

3.2 Performance of S.C.O.T.

S.C.O.T. columns are well established as efficient columns in which the packing is attached to the column wall rather than filling the entire column as in conventional packed columns. Columns from the Perkin Elmer corporation were obtained with coatings of both polar and non-polar phases. This provided columns with a broad range of selectivities for resolution of the 40-component mixture. The number of compounds separated by each of the S.C.O.T. columns is listed in Table 5. Although columns with different lengths were tested, data from only the optimal column lengths are reported. Also included in the table is the analysis time required to elute the last component of the mixture, o-dichlorobenzene. However, care should be used in the interpretation of analysis time versus number of compounds resolved, since different flow and program rates were often used to optimise a particular column.

TABLE 5.

	Column length (m)	Liquid phase	Number of compounds resolved from 40-component mixture.[a]	Analysis time to elute o-dichlorobenzene[a] (mins)
S-1	45.75	MBMA	35	46[b]
S-2	30.5	Carbowax 20M	29	41
S-3	30.5	OV 1 silicone	30	44
S-4	30.5	OV 17 silicone	31	42
S-5A	30.5	Ucon LB550X	36	55
S-5B	45.75	" "	37	65
S-5C	61.0	" "	37	84
Combination columns:				
S-6	30.5	Ucon LB550X +Carbowax 20M	30	54
S-7	30.5	Ucon LB550X + MBMA	35	39

[a] Care must be taken in the interpretation of number of compounds resolved versus analysis time since different flow and program rates may have been used to optimise a particular column.

[b] Hydrogen was used as the carrier gas at a flow rate of 4 cc/min, in place of the usual helium.

<u>Performance of S.C.O.T. columns</u>

Some general observations are pertinent with respect to the overall performance of the S.C.O.T. columns. All of the columns tested resolved the xylene isomers, and most other alkylbenzenes in the mixture; for example, separation of the aromatic group of compounds is illustrated for the Carbowax 20M column in Figure 4. Carbowax 20M was also the only column which gave an acceptable peak shape for polar compounds, as shown in Figure 5. Both methanol and acetaldehyde tailed with varying degrees of severity on all of the other S.C.O.T. columns, OV 1, and OV 17 being the worst. The tailing of alcohols observed with the Ucon LB550X column, although less severe than the OV silicones, was nevertheless quite marked as can be seen in Figure 6. On this basis it would be tempting to select the Carbowax column for further testing, however, this same column was not as efficient as the Ucon when attempting to resolve the halocarbon group of compounds. This point is well illustrated by a comparison of Figures 7, and 8, where all nine components in the mixture are completely resolved on the Ucon column but several pairs co-chromatograph on the Carbowax. Since this trend of superior resolution for the Ucon column was observed with each class of compound in Table 1, it was decided to set aside this column for additional investigation.

The first approach was to determine the optimal conditions for resolving the 40-component mixture with Ucon columns of different lengths.

Vapor samples of the test mixture were therefore chromatographed under a variety of conditions on S.C.O.T. columns of 30.5, 45.75, and 61.0 meters coated with Ucon LB550X. The separation acheived on the 30.5m column is illustrated in Figure 9; the main chromatogram is for a program rate of 4°/min, while the smaller inserted chromatogram represents a slower programming rate of 2°/min which clearly improves the resolution. This is particularly obvious for the methanol peak (Number 1) which was previously obscured under the group of peaks 8A-21, but at the slower program rate is now visible as a broad asymmetric peak. Increasing the length of the column to either 45.75, or 61 meters only slightly improves the resolution as illustrated in Figures 10, and 11,respectively. With the added disadvantage of a much longer analysis time. The broad tailing of the acetaldehyde peak (Number 4) is especially noticeable on all three Ucon columns, clearly if this type of column is to be a serious candidate then the general poor symmetry of polar compounds must be reduced or largely eliminated.

Two attempts were therefore made to solve this problem. In the first, five separate 10ul injections of bistrifluoromethylsilyl-acetamide (a known silylating agent for blocking the active sites on chromatographic supports) were injected into the 30.5m column. During this time the column was heated isothermally at 100°C, with carrier gas flowing but disconnected from the detector. After purging with carrier gas for two hours the column was reconnected to the detector and a sample of the test mixture was injected for comparison. Unfortunately, no improvement in the tailing of either acetaldehyde or methanol was observed. In the second experiment the column was purged at 50°C for six hours with carrier gas saturated with trimethylchlorosilane (another more potent silylating agent) by passage through a bubbler filled with the liquid reactant. After this treatment the column was reconditioned as described in Section 2.5, and then tested with the injection of a polar mixture. Only a very slight improvement in the shape of the acetaldehyde peak was noted, and the methanol peak shape remained unchanged. Presumably, reflecting the greater acidity of the methanolic proton. From these unsuccessful experiments it was decided to halt further work on the S.C.O.T. Ucon columns and instead prepare a capillary coated with the same phase as a possible method of reducing the tailing of polar compounds.

3.3 Combination of S.C.O.T. columns.

Various combinations of S.C.O.T. columns, listed in Table 3, have also been tested to see if two phases in series might improve on the resolution so far achieved with the Ucon phase. In these experiments two 15.25m columns, coated with different liquid phases, were connected together with low dead volume " Swagelock " unions. Pairs of columns were tested in both directions so that sample was first exposed to phase 1 followed by phase 2, and then vice versa.

Surprisingly, none of the combination columns improved the overall separation of the 40-component test mixture compared with the single Ucon S.C.O.T. column; although, as might be expected, for some pairs of compounds in the mixture there was an improvement in resolution. The performance of the more successful combinations are illustrated in Figure 12, with the combination Ucon LB550X/Carbowax 20M, and in Figure 13 with Ucon LB550X/MBMA. As noted in Table 5, this latter combination is almost equivalent to the performance of a 30.5m Ucon column, and it is therefore unlikely that columns prepared with mixed phases of those tested so far would offer any special advantage.

3.4 Performance of Open tubular columns.

Although open tubular or capillary columns have the greatest efficiency of the column types evaluated in this study, they are, nevertheless, susceptible to the same basic problem with respect to the asymmetric peak shape of polar compounds observed with both packed and S.C.O.T. columns. As a consequence, many of the columns listed in Table 4, were rejected as serious candidates due to severe tailing of methanol and other polar components in the test mixture. Conversely,on some of the columns, e.g. Triton X-305, polar compounds chromatographed as quite symmetrical peaks whereas aromatics were either unresolved or rather broad. The unsuccessful columns and the reasons for their preliminary rejection are listed in Table 6.

Some phases were unexpectedly disappointing, including OV 275 a very new phase, and the well established phase, Dinonyl phthalate. The initial selection of Dinonyl phthalate was suggested by tables of Retention Indices, which implied that this particular phase might separate almost all of the compounds listed in Table 1. Figure 14, demonstrates dramatically that this optimistic prediction is not realised in practice.

Because the Polyalkylene glycol or Ucon series of phases had previously shown a high selectivity for resolution of the 40-component test mixture, capillary columns were preferentially coated with these phases. Freshly coated capillaries were generally subjected to preliminary testing by injection of vapor samples for each class of compound listed in Table 1.

TABLE 6.

Capillary columns with unsatisfactory performance.

	Column	Number of compounds resolved	Comments.
C.12	PMP	24	Minimum operating temperature of 125°C.
C.13	AN600	32	Polar compounds tail badly
C.14	OV 275	28	Aromatics and isomers poorly resolved.
C.15	DEGS	12	Column not efficiently coated
C.19	Dinonyl phthalate	31	Resolution and peak symmetry poor.
C.20	Triton X-305	25	Aromatics and Halocarbons poorly resolved.
C.3	Ucon LB 280X	31	Methanol tails badly.
C.4	Ucon LB550X	31	" " "

These tests were particularly useful since they not only rapidly established the separation characteristics of each column, but clearly indicated which individual compounds were susceptible to adsorption by the column. For example, Figure 15, illustrates the satisfactory peak shape obtained with alcohols on a Ucon capillary (C.7); in contrast to Figure 16 where the same alcohol mixture is chromatographed on a column coated with AN600 silicone (C.13). The performance of the above Ucon column for some of the other classes of compounds is shown in Figure 17 (Ketones), Figure 18 (Esters), Figure 19 (Aldehydes)and Figure 20 (Aromatics). Significantly, peak symmetry is good for each class of compound, and each component is well separated from related homologues. Benzene and toluene have been included in the class mixtures as internal standards, which is a useful technique for the subsequent determination of accurate relative retention times.

The overall performance of the various capillary columns, in terms of analysis times and resolution of the test mixture, is reported in Table 7. Suprisingly, Carbowax 20M, which is chemically closely related to Ucon, only resolved 30 of the 40-component mixture. This is partly explained by a minimum operating temperature of 60^{O}C, where the phase which is a low melting solid first becomes liquid. This causes bunching and early elution of the lower boiling compounds of the mixture, as is most obvious in Figure 21. This same problem was observed with the Polymetaphenoxylene phase which has a practical minimum operating temperature of 125^{O}C and

TABLE 7.

Performance of capillary columns.

Column.	Phase.	Number of compounds resolved.	Analysis time (mins).
C.1	Ucon 50HB2000	35	65
C.2	Ucon 50HB5100	34	46
C.5 [a]	Ucon50HB2000 + UconLB1200X	35	60
C.6 [b]	" " "	37	37
C.7 [c]	" " "	38	45
C.8 [d]	" " "	38	68
C.9	Ucon 50HB2000 + DEGS	28	39
C.10	Ucon 50HB2000 + PPE [e]	28	38
C.11	Carbowax 20M	30	36
C.16	Ucon 50HB2000	30	36
C.17	Ucon LB1200X	29	32

[a] Ratio of phase mixture: (7:3), [b] (8.5:1.5), [c] (9.1), [d] (9.1).
[e] Polyphenylether 6 ring.

leads to even poorer resolution of the early components. The consistent superior resolution of the Ucon columns is quite evident. However, there are two distinct types of Ucon, the LB series, and the HB series of which the latter is the most polar. In practice, the most efficient capillaries are prepared from the highest polarity Ucon, such as 50HB2000, in contrast to the less polar LB280X and 550X. This is well illustrated in Figure 22, where only 31 compounds of the test mixture are resolved on a LB550X capillary column, and methanol (peak number 1) has a pronounced tail. Nevertheless, the LB Ucons do have some virtues; analysis times are, in general, faster and certain previously unresolved or partially resolved components in the mixture do show an improvement in separation, (e.g toluene and tetrachloroethylene).

Experiments were therefore designed to try and incorporate some of the desirable characteristics of the LB series with the proven performance of the HB Ucons. The more successful of these experiments led to the development of a mixed phase Ucon column in which 10-30% of the Ucon LB1200X was mixed with Ucon 50HB 2000 as the primary phase. From Table 7, it is clear that the most effective mixture , in terms of the number of compounds resolved and the total analysis time, is one containing 10% of the Ucon LB 1200X. Although resolution may be improved for some compounds if greater concentrations are used, in other cases the different selectivities of the two phases combine adversely to cause other peaks to merge together. Based on these results a column coated with the mixed Ucon phase (90% Ucon 50HB2000 + 10% Ucon LB 1200X) has been selected for the column test period.

The separation of the 40-component test mixture on this column is shown in Figure 23. Two pairs of compounds still remain unresolved despite the improved performance of the mixed Ucon column; these are Methyl chloride (24), and 1,3-Butadiene (8), and also Methylene chloride (7A), and Ethyl acetate (18). In addition, Toluene (10A), and Tetrachloroethylene (26) are only marginally resolved. It might be thought that the separation of these pairs could be further improved by simply increasing the length of the column. To test this suggestion, two 91.4 meter Ucon capillaries were joined together in series to make a column of total length 182.8 meters (Column C.8) Although this did improve the separation of partially resolved pairs, such as Toluene and Tetrachloroethylene, the two other pairs of unresolved compounds could still not be separated, (See Figure 24). This implies that the selectivity of the Ucon phases for these particular compounds is inadequate and merely increasing the number of theoretical plates offers no special advantage. In fact, there is a penalty to be paid in the form of a much longer analysis time.

An alternative approach to resolving these difficult pairs is to modify the Ucon phase by the addition of chemically different phases. Therefore, capillary columns were coated with Ucon 50HB2000 to which the following phases were separately added at a concentration of 10% by volume, Diethylene glycol succinate, Polyphenylether 6 ring, and Silar 10C. Unfortunately, the addition of the Silar 10C was generally unsuccessful with almost all the components chromatographing as unsymmetrical peaks. Even the other two phases were disappointing, and in each case the overall resolution was inferior to that obtained with the mixed Ucon phase.

3.4.1 Optimisation of capillary column performance

With the selection of the mixed phase Ucon column for the test period, experiments were performed to assess its efficiency under varying conditions of temperature, carrier gas , and flow rate. These results are summarised in Table 8. Several conclusions are immediately obvious, of which the most important is that the total analysis time with isothermal conditions may be reduced by as much as 30% when hydrogen is substituted for helium as the carrier gas. With the column held isothermally resolution of the 40-component mixture deteriorates as the temperature is raised with a concomitant decrease in analysis time. For example, the total analysis time can be halved by operating the column isothermally at 85°C as opposed to 60°C, for the same hydrogen flow rate of 5cc/min. Although the number of compounds resolved drops from 30 to 25.

As might be expected, increasing the carrier gas flow rate reduces analysis time, but fortunately only with a slight loss of resolution. Clearly from Table 8, at a temperature of 60°C, flow rates in the 10cc/min range provide the best compromise between resolution and analysis time. Most significant is the observation that at any isothermal temperature 39 of the compounds, listed in Table 1, are eluted in less than half the

TABLE 8

Effect of varying column flow rate, temperature, and carrier gas.

Temperature °C	Flow Rate	Carrier Gas	Analysis Time	Number Resolved[a]
60	5cc/min	Hydrogen	83 min.	30
70	" "	"	66 min.	28
80	" "	"	51 min.	26
85	" "	"	37 min.	25
60	7.5cc/min	"	70 min.	31
70	" "	"	57 min.	28
80	" "	"	37 min.	26
60	10cc/min	"	42 min.	30
70	" "	"	29 min.	26
80	" "	"	25 min.	23
Program:*	5cc/min	Hydrogen	33 min.	35
25°C to 120	7.5cc/min	"	30 min.	35
@ 4°/min.	10cc/min	"	27 min.	32
Program:*				
25°C to 120	5cc/min	Helium	37 min.	37
@ 4°/min.	10cc/min	"	34 min.	33
85	5cc/min	Helium	51 min.	27
60	10cc/min	"	69 min.	34
70	7.5cc/min	"	62 min.	30
80	" "	"	45	28

N.B. Column was 91.4m by 0.05cm i.d. capillary coated with 85% Ucon 50HB2000/15% Ucon LB 1200X. This mixture is less efficient than the 90/10 Ucon combination but a slightly faster column.

* Held for 6 minutes at 25°C before programming.

[a] 40- component vapor mixture

total analysis time. For example, at 70°C and a hydrogen flow rate of 10cc/min it takes only 12 minutes to elute 39 compounds including mesitylene, but an additional 17 minutes to elute the last component, o-dichlorobenzene.(See Figure 25) Obviously, if the o-dichlorobenzene is not a significant or important component of spacecraft atmospheres, this would considerably simplify the analytical requirements.

In summary isothermal operation has two distinct disadvantages, considerably fewer compounds are resolved, and the analysis time is much longer at any fixed flow rate. This is illustrated in Figure 26, where only 30 of the 40 test compounds are resolved, and the analysis time is increased by almost 70% to 76 minutes compared with temperature programming of the same column. (See Figure 23)

When the column is temperature programmed the same general trends apply: i.e faster flow, or program rates decrease analysis time at the expense of resolution. Interestingly, changing the carrier gas to hydrogen only reduces analysis time by 10-15% compared with the 30% reduction noted for isothermal conditions. The separation of the forty test compounds is achieved within 45minutes at a program rate of 4°/min, and a helium flow rate of 6cc/min. However, after the elution of mesitylene (12), another 14 minutes are required to elute the last component, o-dichlorobenzene. Once again, elimination of this component from the test mixture would offer an approximately 30% saving in overall analysis time.

4.0 Column preparation for column test period.

Three columns have now been coated with the mixed Ucon phase in preparation for column testing. The proceedure for coating the 91.4m by 0.05cm i.d columns was standardised as follows:-

Coating solution:

9.0grams of Ucon 50 HB2000 +
1.0 gram of Ucon LB1200X

Dissolve in 100 ml of methanol.

A 10 ml 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 6psi. The velocity of the coating solution through the column was adjusted by means of the flow controller to 3 mm/sec. After the solution had eluted from the column,the column was reversed and a further 2 ml of the coating solution was forced through the column in the opposite direction. After this second aliquot had passed through the column, 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 1 ml of vapor sample of halocarbons. Satisfactory resolution of methylene chloride, methyl chloroform, and carbon tetrachloride was taken as the first indication that the column was acceptable. To confirm performance the entire 40-component mixture was injected as a 1 ml vapor sample.

At least 38 compounds in the mixture should be satisfactorily resolved with the following operational parameters:

Helium flow rate: 5 cc/min.
Program sequence: Isothermal for 6 mins at 25°C then program at 4°/min to 120°C, and hold until o-dichlorobenzene is eluted.
Column injector temperature: 250°C.
Hydrogen flame detector temperature: 300°C.

Acceptable or satisfactory resolution (R), for a pair of closely spaced peaks , can be defined on a chromatographic basis from the following relationship.

$$R = 4 (X_2 - X_1)/Y_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where X_1 is the retention time of the first component, and X_2 is the retention time of the second component. Y_2 is is the base peak width of the second component. It is assumed that for very close peaks that $Y_1 = Y_2$. Column efficiency defined by the number of theoretical plates, (N) is related to resolution as follows:-

$$R = N^{\frac{1}{2}} (1 - X_1/X_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Refering to Figure 23, we can calculate the resolution for different components in the mixture. For example, considering dichlorofluoromethane (4A), and acrolein (5) then, X_1 = 58mm, X_2 =60mm, and Y_2 = 2mm,

hence:

$$R = 4(60-58)/2 = 4.$$

A resolution of 4 represents 98% separation of acrolein and dichlorofluoromethane. Similarly, we can calculate a resolution of 2 for toluene (10A) and tetrachloroethylene (26), or about 50% separation.

5.0 Sampling considerations.

All vapor samples were injected with a 10 ml gas syringe, and the maximum sample size which can be injected into the 91.4m by 0.05cm i.d columns was found to be 1 ml. The injection of larger sample volumes causes progressive loss of resolution, particularly for partially unresolved pairs. However, it should noted that where injections of sample are made with a more efficient gas sampling valve, this maximum sample volume may be significantly greater. Capillary columns with larger internal diameters, e.g 0.076cm should permit a further increase in sample size; although these columns have not been as extensively investigated during the course of this study.

6.0 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 maximum flow rate was set not to exceed 10 cc/min. Only two carrier gases have been used in the present experiments, helium and hydrogen. Helium has been used as the prefered gas, however, hydrogen is attractive since it reduces the total analysis time. Carrier gas separators have been developed to handle both types of carrier gas. Membrane or jet separators are perhaps the most developed for helium, while the Palladium/ Silver separator is particularly useful for hydrogen. 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.

Since there are two pairs of compounds unresolved by the test column, there is the possibility that this may compromise the mass spectral identification. The mass spectra for selected components in the mixture are listed in Table 9. Only the ten most abundant fragment ions are included in Table 9, and it is to be noted that isopropanol (molecular weight = 60), methyl chloroform (molecular weight = 132), and carbon tetrachloride (molecular weight = 152) do not give rise to molecular ions.

For the chromatographically unresolved pairs, methyl chloride and 1,3-butadiene, and methylene chloride and ethyl acetate there is clearly no problem in mass spectrally resolving these mixtures. 1,3-butadiene has a characteristic base peak at m/e 39, while there is no frament ion with a mass of 39 produced from methyl chloride. Similarly, ethyl acetate and methylene chloride have base peaks with masses of 43 and 49, respectively, and hence are easily distinquished. The incompletely separated toluene and tetrachloroethylene are also easily determined mass spectrally from their base peaks. (toluene 91, and tetrachloroethylene 164.) Three other compounds in the test mixture are also rather closely bunched on the capillary column, and once again the mass spectrometer would easily confirm their identification. Thus methyl chloroform is distinquished from carbon tetrachloride by fragment ions at masses 61 and 97, while isopropanol is readily recognised by its base peak at m/e 45.

TABLE 9.

Mass spectra of partially resolved compounds

M/E	RELATIVE INTENSITY %.								
	Methyl chloride.	I,3-Butadiene.	Methylene chloride.	Ethyl acetate.	Methyl chloroform.	Carbon tetrachloride.	Isopropanol.	Toluene.	Tetrachloroethylene.
13	5.4								
14	8.4								
15	72.3								
19							6.6		
26		25.7							
27		67.9		6.1			15.7		
28		45.6		5.5					
29				13.4			10.1		
31							5.6		
35	6.2		12.1		6.8	40.9			7.1
37			3.8			12.7			
38									
39		100.0					5.7	18.7	
41			4.8				6.6		
42				5.1			3.9		
43				100.0			16.6		
44							3.3		
45				15.5			100.0	5.3	
46									
47	7.1		17.8			40.6			18.9
48	3.4		8.7						
49	11.4	8.2	100.0			13.0			
50	100.0	24.5						6.0	

TABLE 9, cont'd.

RELATIVE INTENSITY %.

M/E	Methyl chloride.	1,3-Butadiene.	Methylene chloride.	Ethyl acetate.	Methyl chloroform.	Carbon tetrachloride.	Isopropanol.	Toluene.	Tetrachloro-ethylene.
51	3.8	21.7	30.1					9.6	
52	31.0	10.6							
53		59.3							
54		85.9							
59							3.4		10.7
60					7.3		10.4		
61				15.8	50.3				3.7
62					8.2				
63					17.3			8.7	
65								13.1	
70				10.4					
73				5.1					
82						29.1			7.9
83						18.5			
84			57.7						
86			36.2						
88			5.7	6.9					
90								7.9	
91								100.0	
92								75.6	
93								5.2	
94									33.0
97					100.0				
99					64.5				
101					10.4				
117					18.9	100.0			
119					18.8	96.0			
121						30.3			
129									99.8
130									4.0
164									100.0

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 Ucon phases have, of course, been selected for their 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 Ucon column, and this is reached during temperature programming rather than set isothermally. The column can, of course, be operated at a still lower maximum temperature, and the overall analysis time maintained by increasing the carrier gas flow rate, although with a slight reduction in optimum resolution. Because there so little actual phase in the capillary column there is little or no likelihood that the bleed would interfere with the maintainence of ion source pressure.

7. Column Testing

Column testing was commenced on February 1st, 1975 using the experimental arrangement illustrated in Figure 27. 1 ml vapor samples of the 40-component test mixture are injected every hour by an automatic sample injection valve (Valco Instrument Co, houston, Texas), driven by a air operated solenoid. The actual sample valve configeration is shown in Figure 28. The results of the column test period will be reported separately as specified in the Data Requirements List.

8. 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.

9. FUTURE WORK

Clearly one area which might benefit from additional research is the resolution of the two pairs of compounds which are not separated by the present Ucon test column. The approach to this problem would involve mixing small amounts of liquid phases with known separation characteristics for methyl chloride and 1, 3-butadiene, and also methylene chloride and ethyl acetate. The difficulty with this class of problem is that although one or both pairs of the above compounds may be separated it is not possible, a priori, to be certain that other pairs will not begin to co-chromatograph.

Another area for possible development is the use of very high efficiency packed columns which have only just been reported by Kaiser in Germany. These are claimed to have equivalent efficiencies to capillary columns, and could be especially attractive for the analysis of spacecraft atmospheres if packed with chemically bonded packings with low bleed characteristics.

FIGURE 1

2.74m by 0.127cm packed column.

Durapak Low K.

Helium 6cc/min.

25° for two mins then program
@ 4°/min to 140°C.

Sample: 40 component vapor mixture.

Chart speed 1/4"/min.

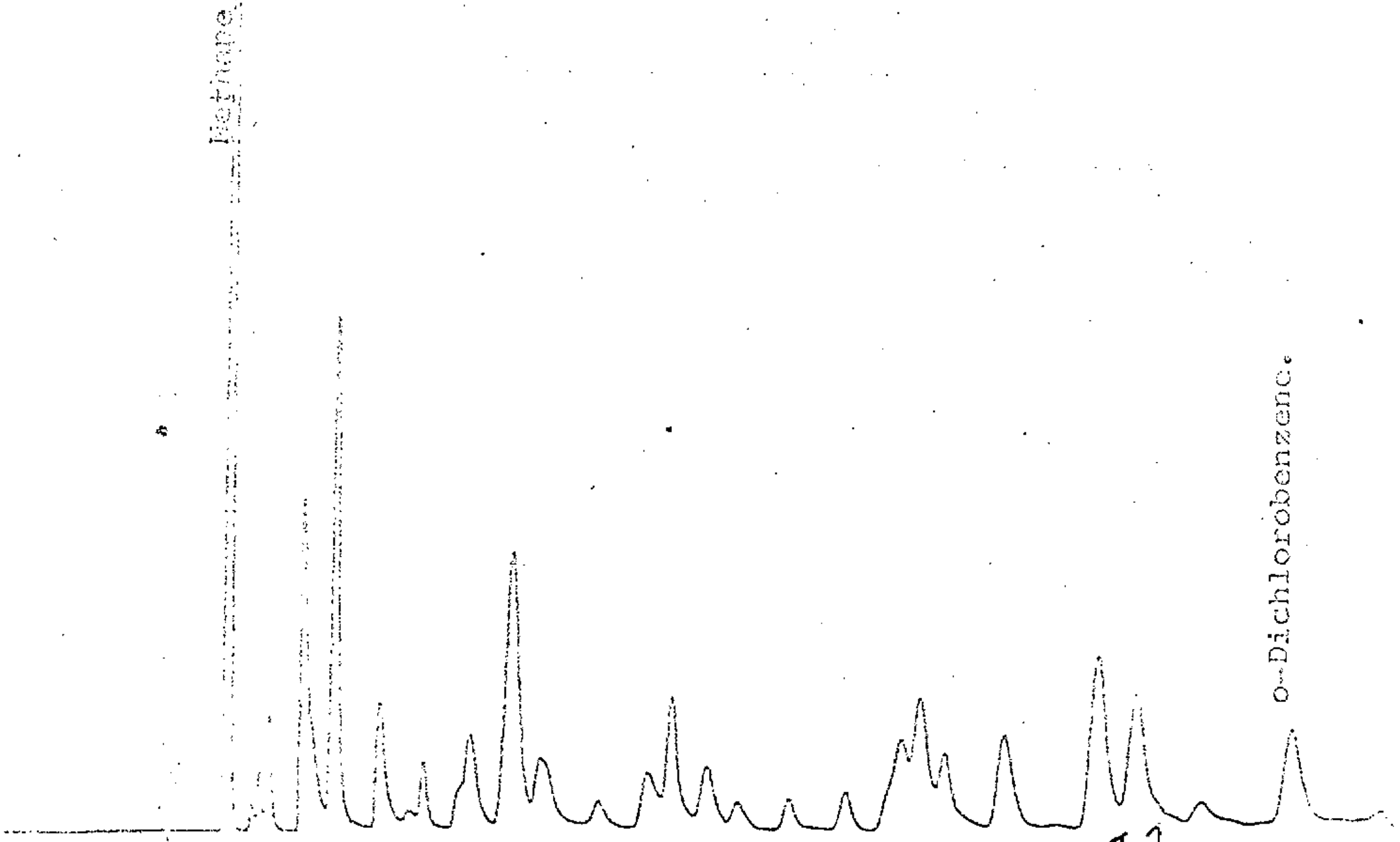


FIGURE 2

4.3 meter by 0.127cm packed column

Durapak Low K. Isothermal 25°for 4mins
then program to 130 @ 4°/min.
Helium flow: 9cc/min.

Sample: 40-component vapor mixture.

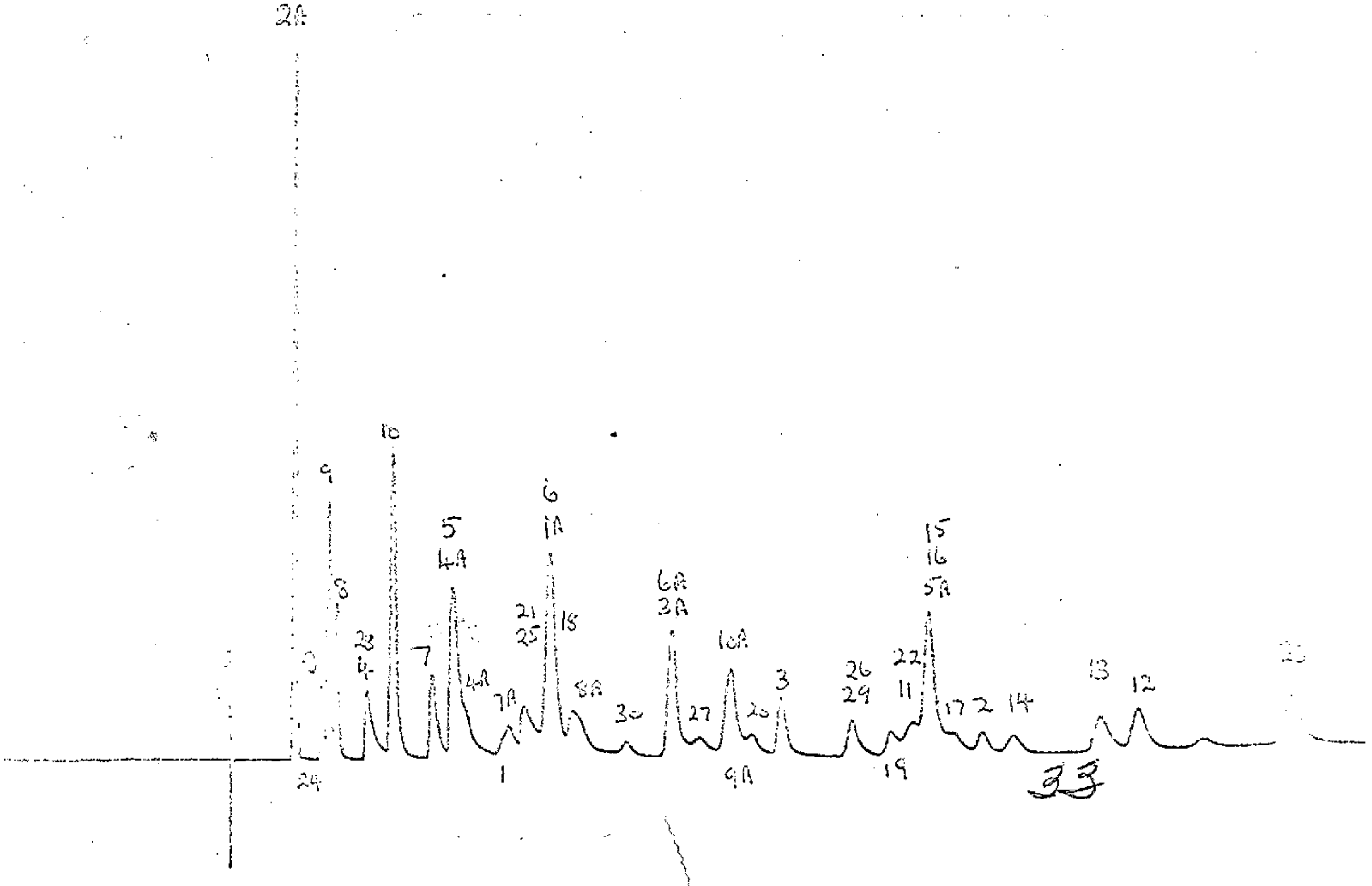
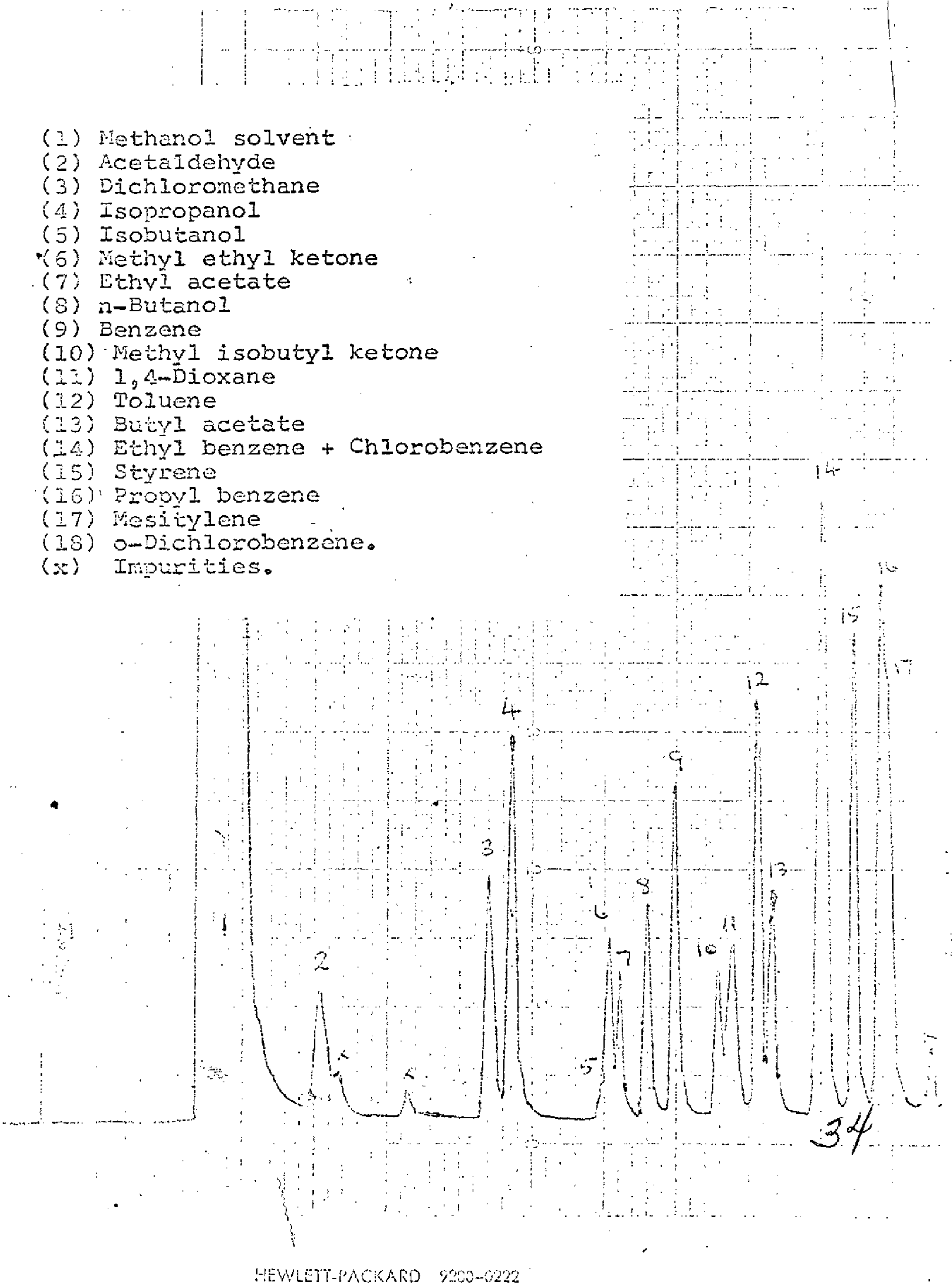


FIGURE 3

Column 2.0 meter by 0.076 i.d packed 2% MPE on 60-80 mesh Tenax-GC. Isothermal 4mins @ 50°, program @ 8°/min to 230°C, then hold for 8mins.

Chart speed 1/4" per minute. Flow rate Helium 7cc/min


(1) Methanol solvent
(2) Acetaldehyde
(3) Dichloromethane
(4) Isopropanol
(5) Isobutanol
(6) Methyl ethyl ketone
(7) Ethyl acetate
(8) n-Butanol
(9) Benzene
(10) Methyl isobutyl ketone
(11) 1,4-Dioxane
(12) Toluene
(13) Butyl acetate
(14) Ethyl benzene + Chlorobenzene
(15) Styrene
(16) Propyl benzene
(17) Mesitylene
(18) o-Dichlorobenzene.
(x) Impurities.

34

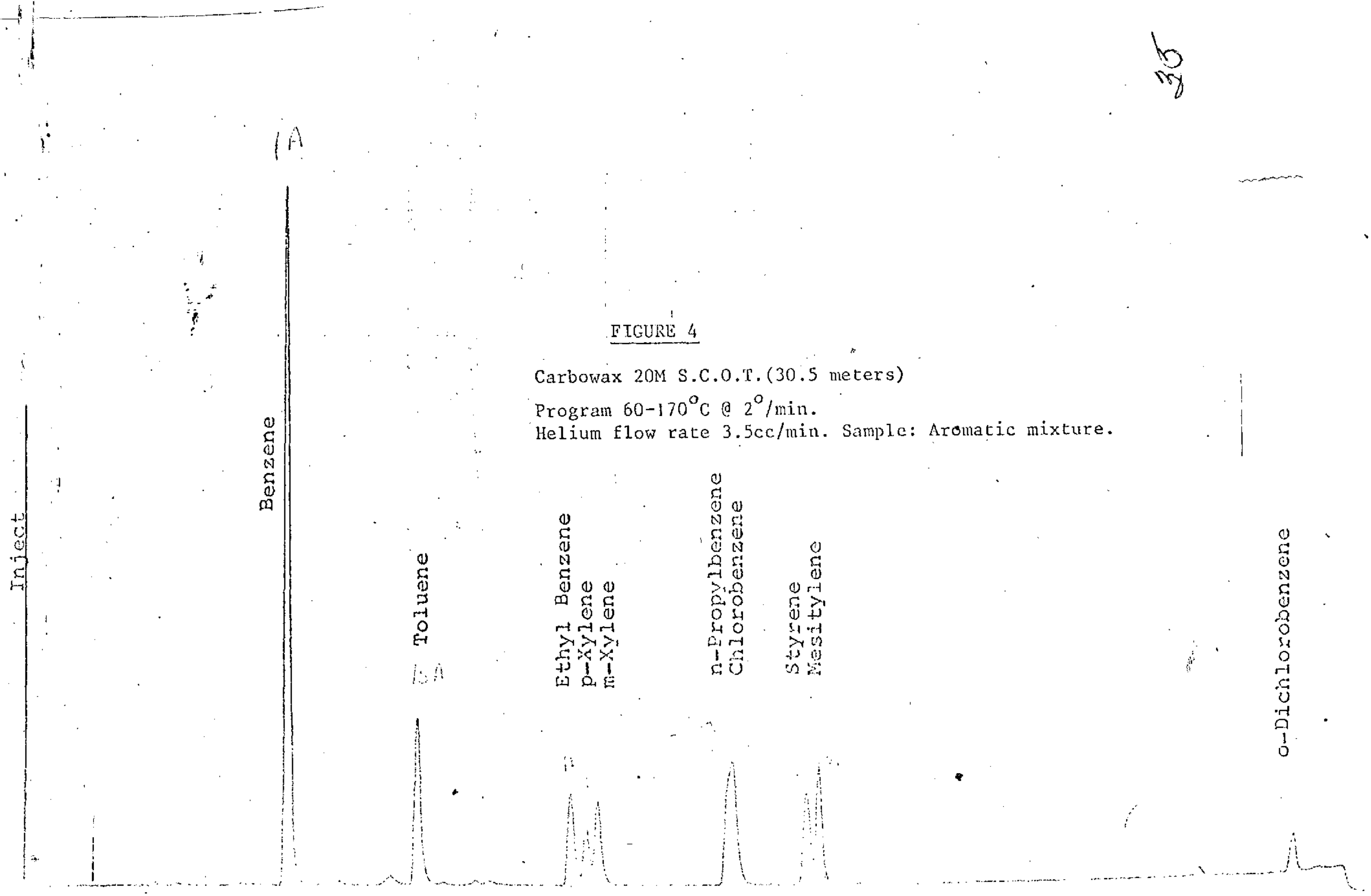


FIGURE 4

Carbowax 20M S.C.O.T.(30.5 meters)

Program 60-170°C @ 2°/min.
Helium flow rate 3.5cc/min. Sample: Aromatic mixture.

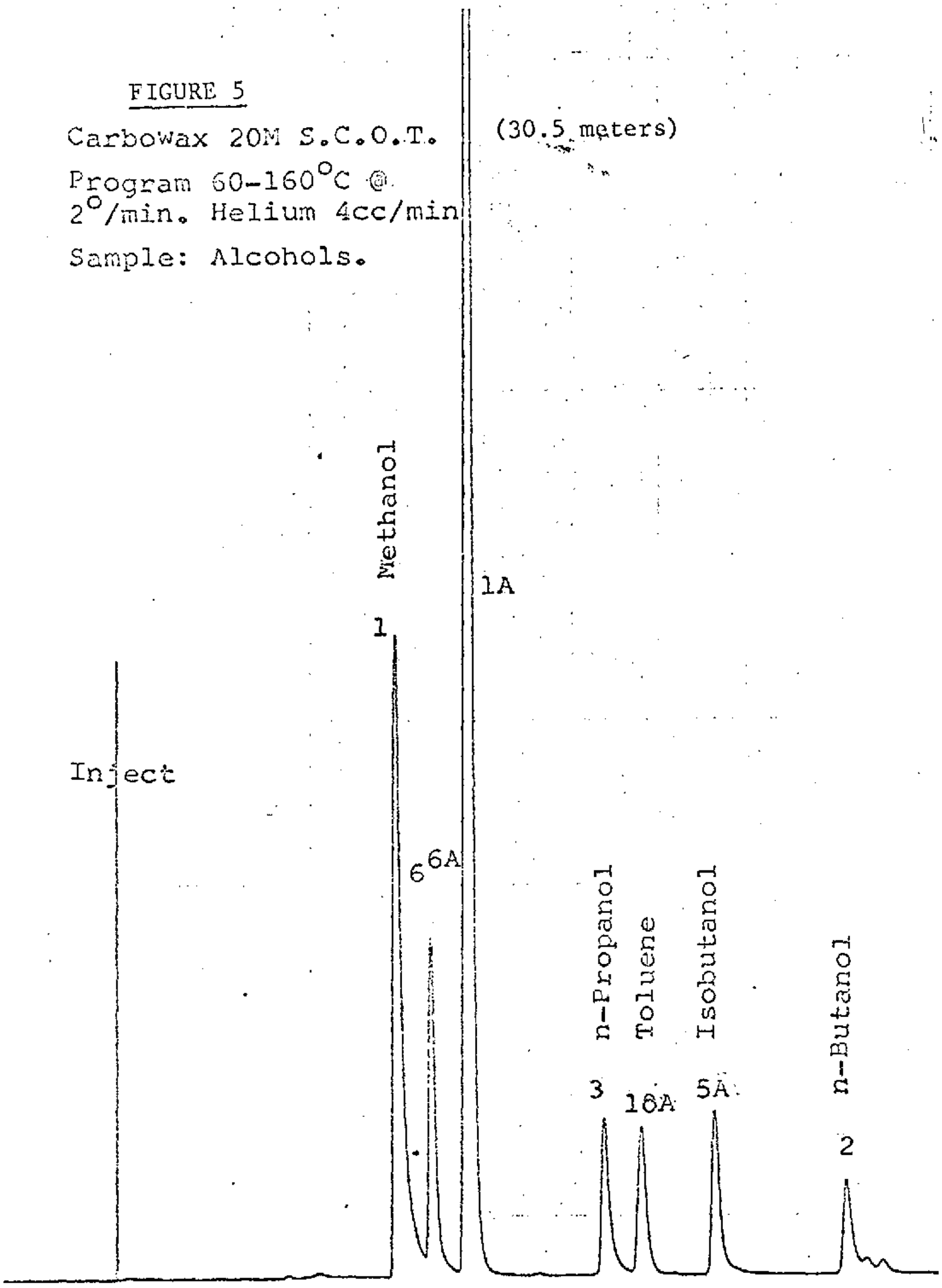


FIGURE 5

Carbowax 20M S.C.O.T. (30.5 meters)

Program 60-160°C @
2°/min. Helium 4cc/min

Sample: Alcohols.

FIGURE 6

30.5 meter LB 550X S.C.O.T.
Isothermal 25°C for 4 mins then program @ 4°/min to 120°C. Helium: 3cc/min.
Chart speed 1/4 /min.

Sample: alcohols.

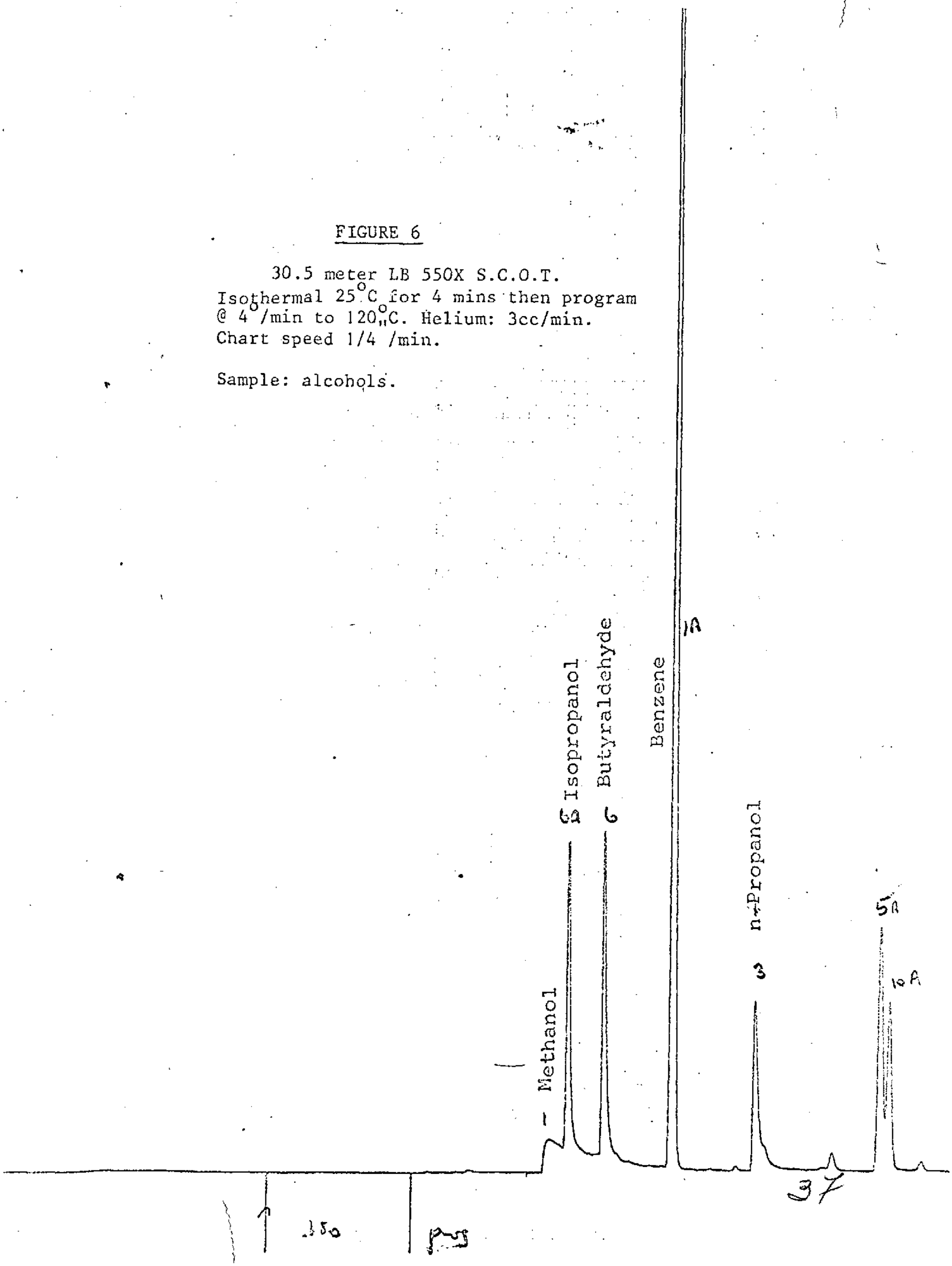
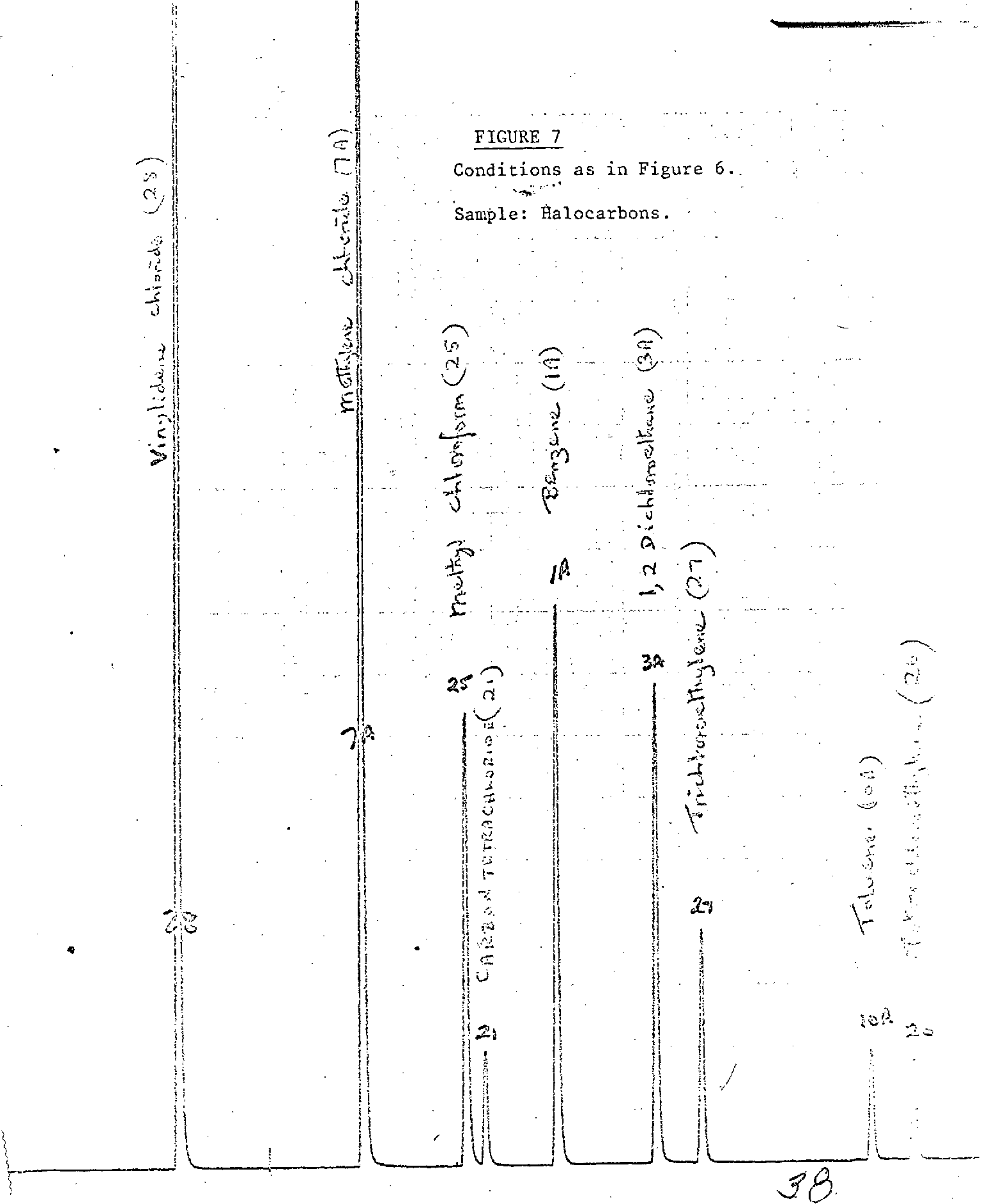


FIGURE 7

Conditions as in Figure 6.

Sample: Halocarbons.



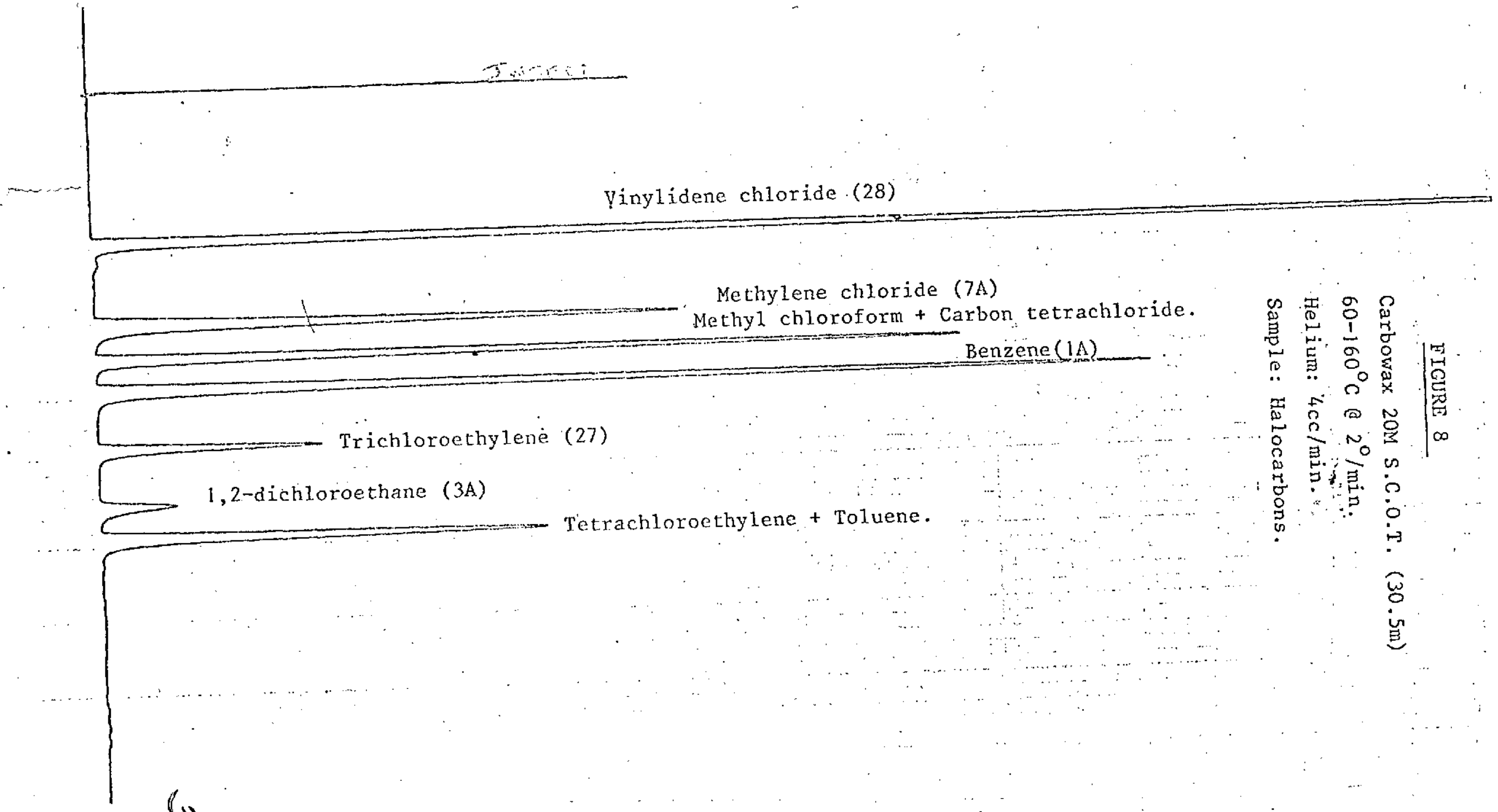
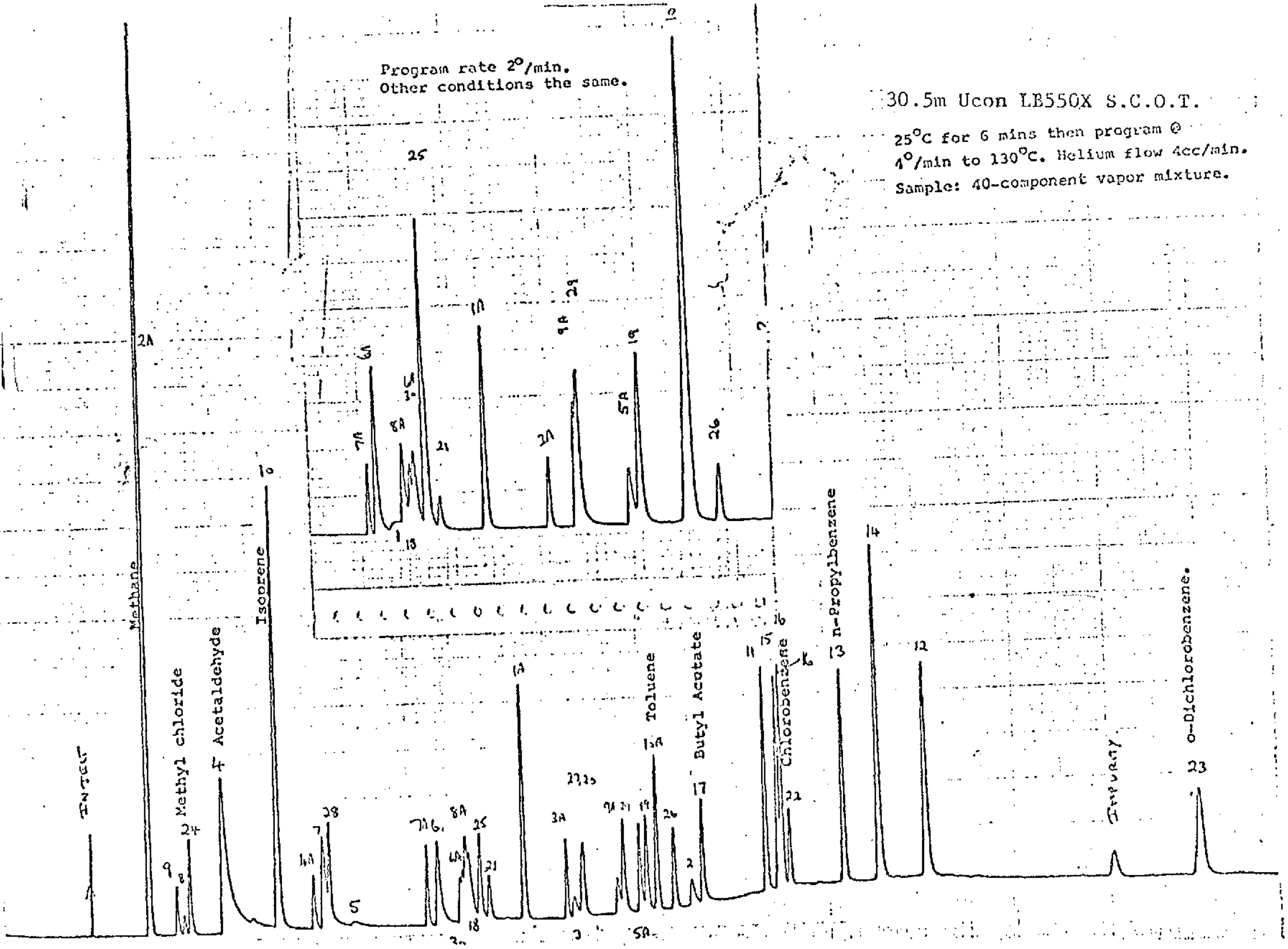


FIGURE 8

Carbowax 20M S.C.O.T. (30.5m)
60-160°C @ 2°/min.
Helium: 4cc/min.
Sample: Halocarbons.

FIGURE 9.



30.5m Ucon LB550X S.C.O.T.

25°C for 6 mins then program @ 4°/min to 130°C. Helium flow 4cc/min.
Sample: 40-component vapor mixture.

FIGURE 10

45.75m Ucon 550X S.C.O.T.

Isothermal 25°C for 4mins then program @ 2°/min to 120°C. Helium: 4cc/min.
Sample: 40-component vapor mixture.

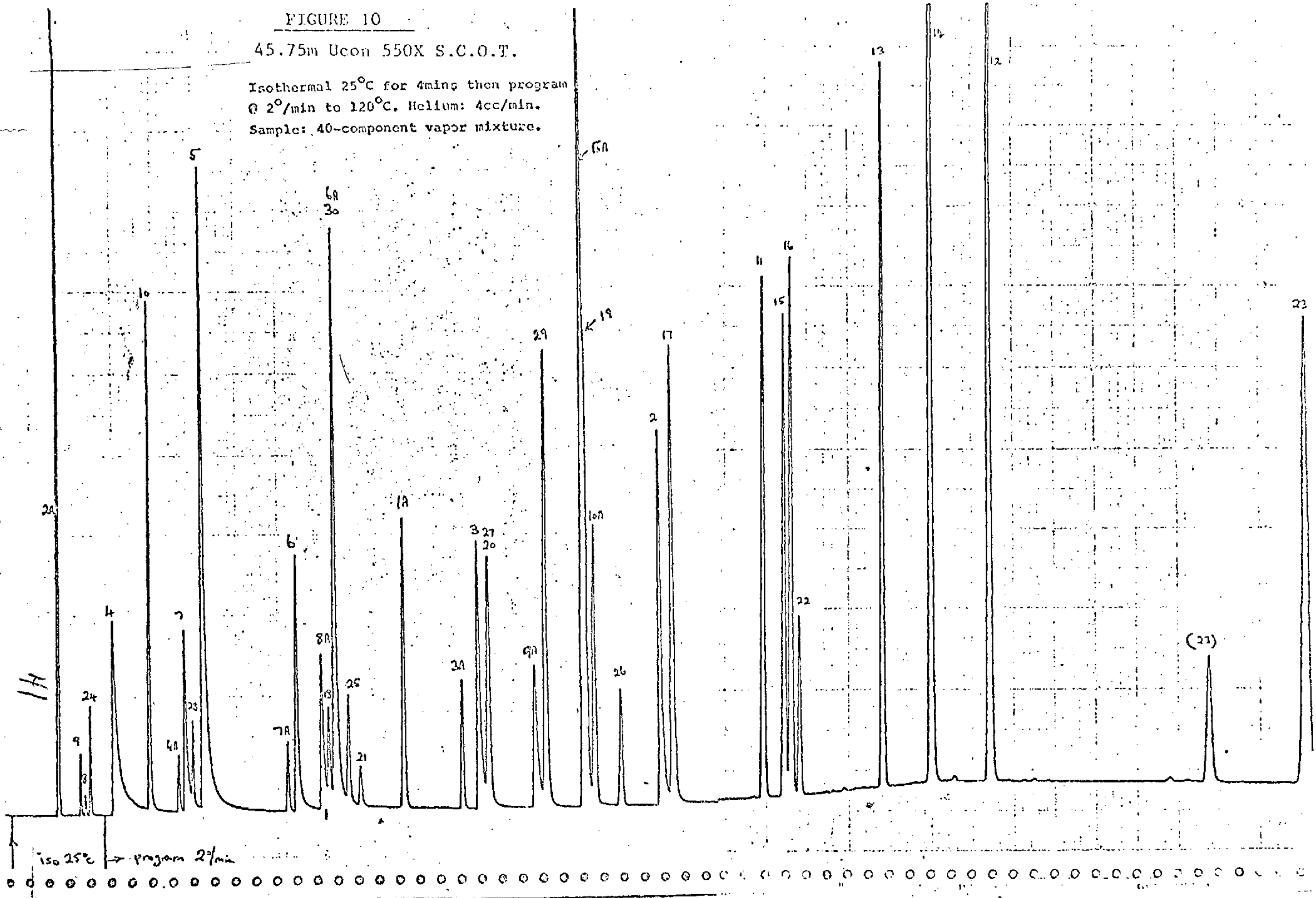
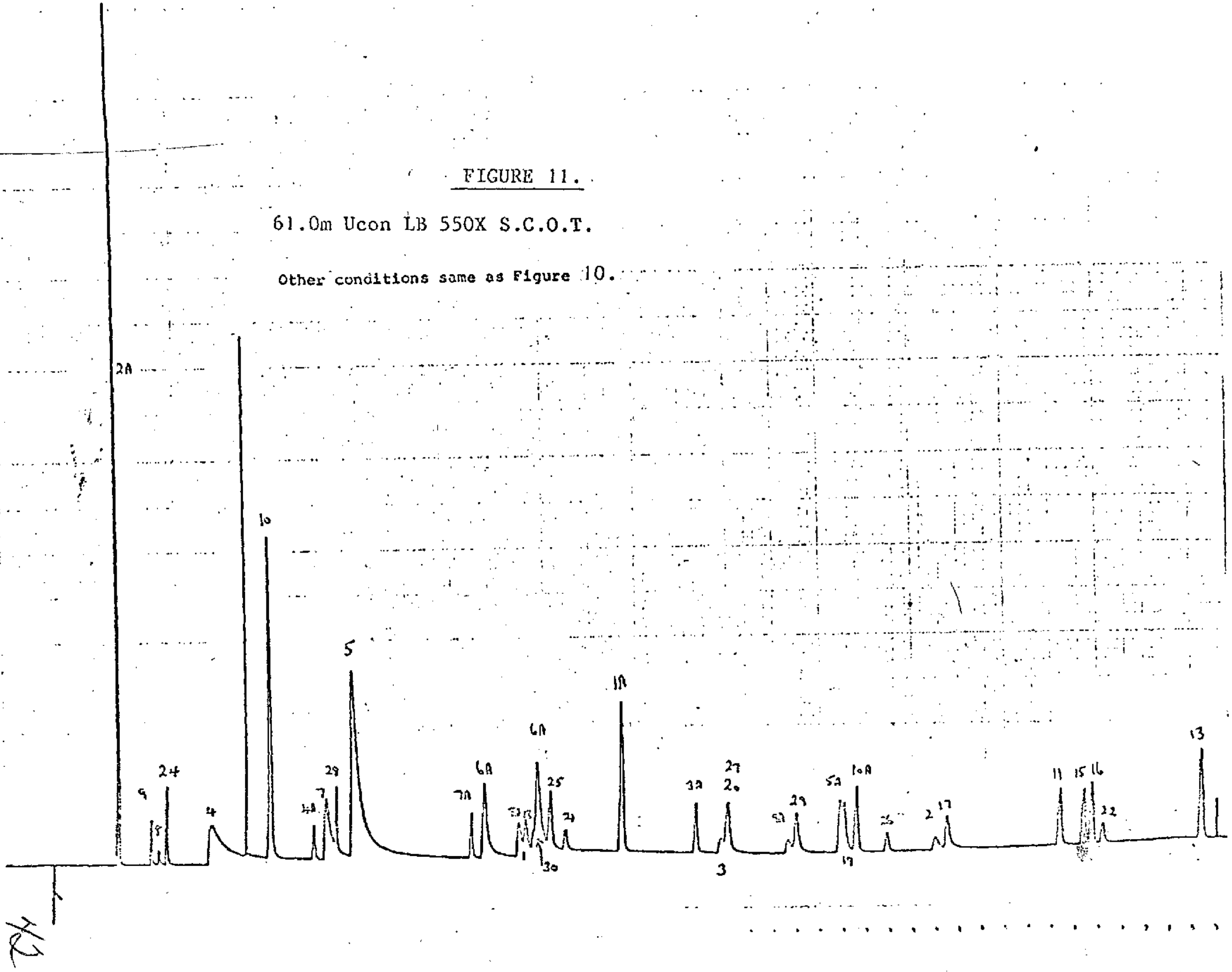


FIGURE 11.

61.0m Ucon LB 550X S.C.O.T.

Other conditions same as Figure 10.



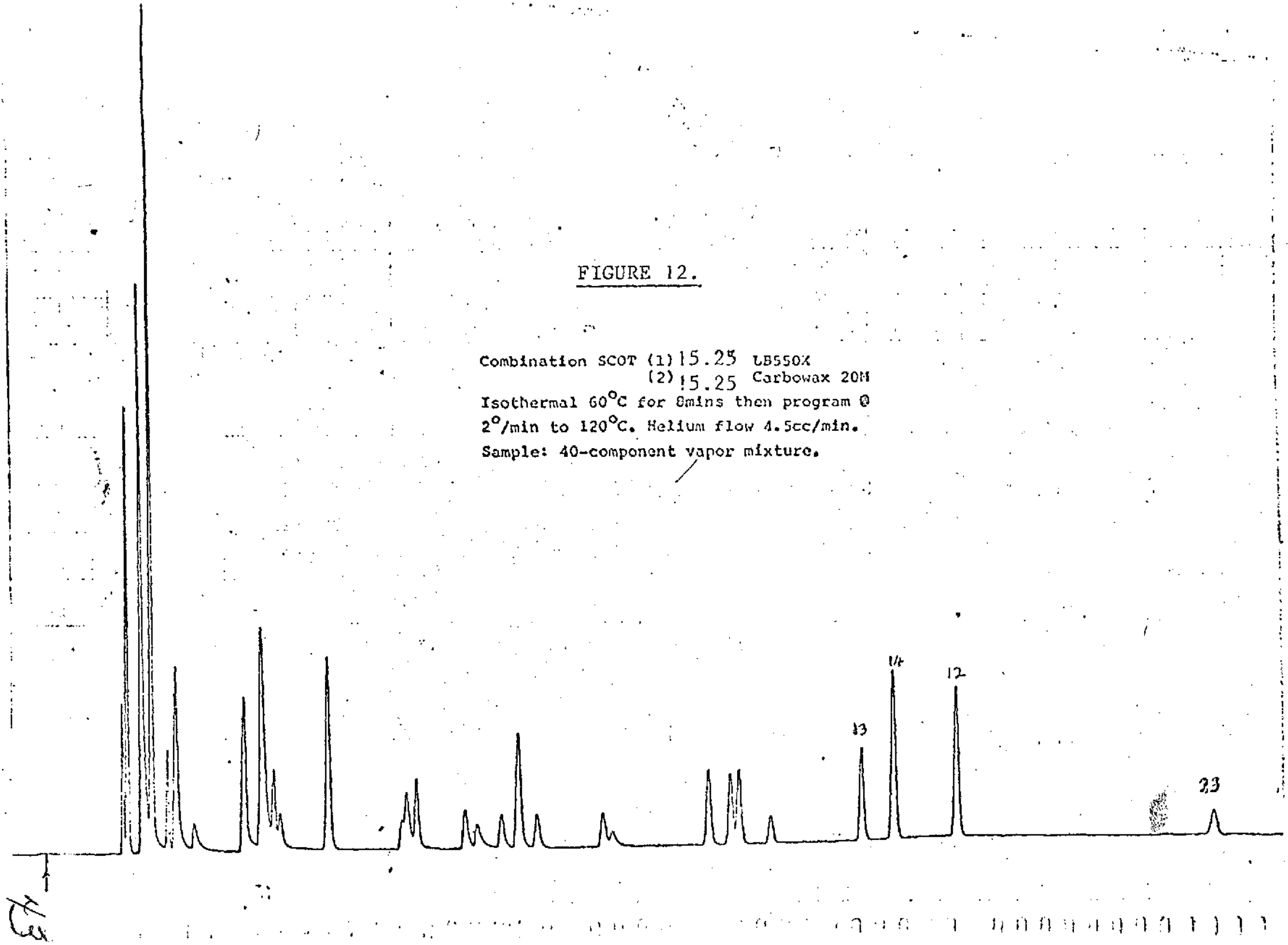


FIGURE 12.

Combination SCOT (1) 15.25 LB550X
(2) 15.25 Carbowax 20M
Isothermal 60°C for 8mins then program @ 2°/min to 120°C. Helium flow 4.5cc/min.
Sample: 40-component vapor mixture.

FIGURE 13.

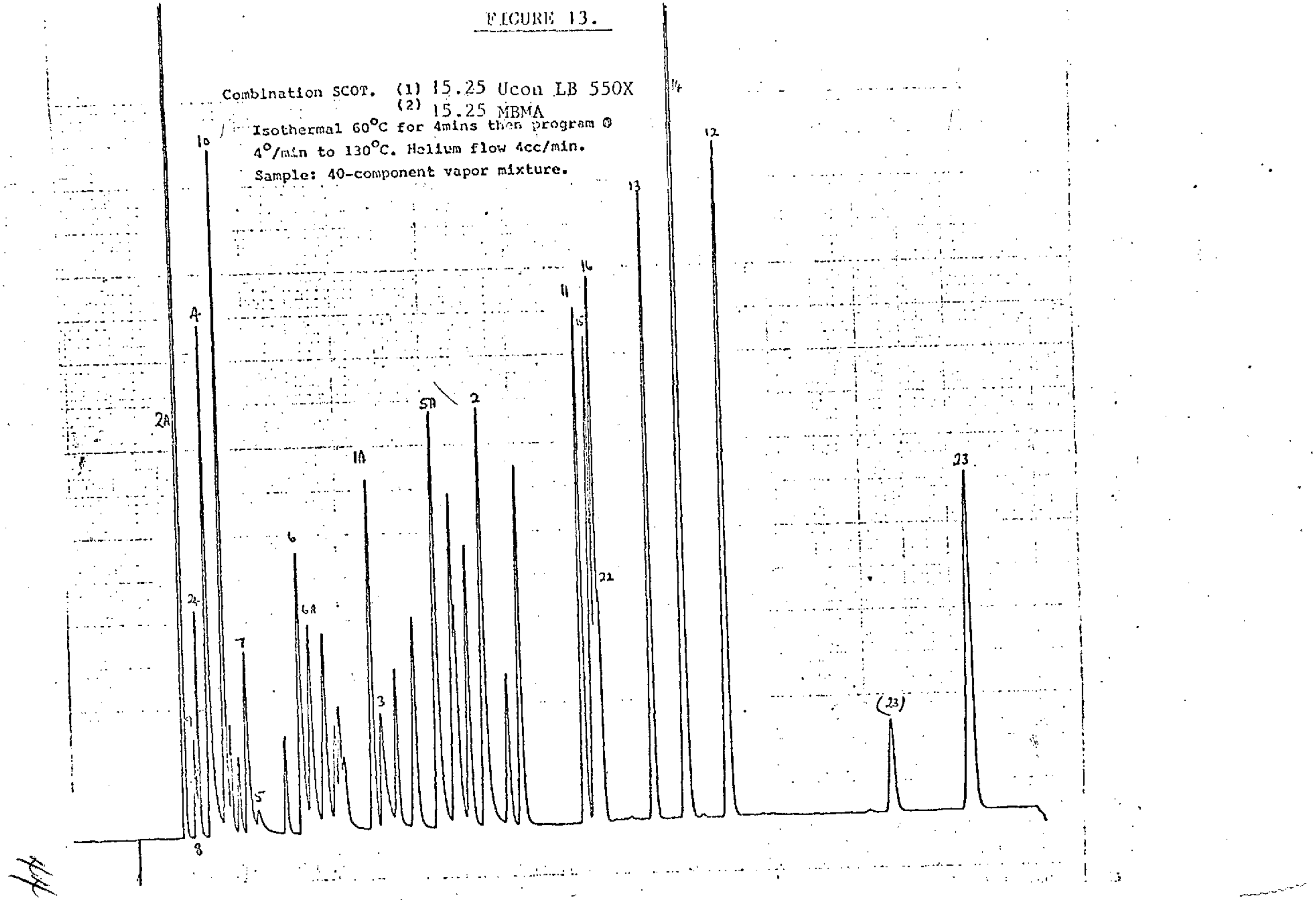

Combination SCOT. (1) 15.25 Ucon LB 550X
(2) 15.25 MBMA
Isothermal 60°C for 4mins then program @
4°/min to 130°C. Helium flow 4cc/min.
Sample: 40-component vapor mixture.

FIGURE 14.

30.5 meter Dinonyl phthalate capillary column

Program @ 4°/min from 25° to 110°C

Helium flow rate : 6cc/min.

Sample : 40-component mixture.

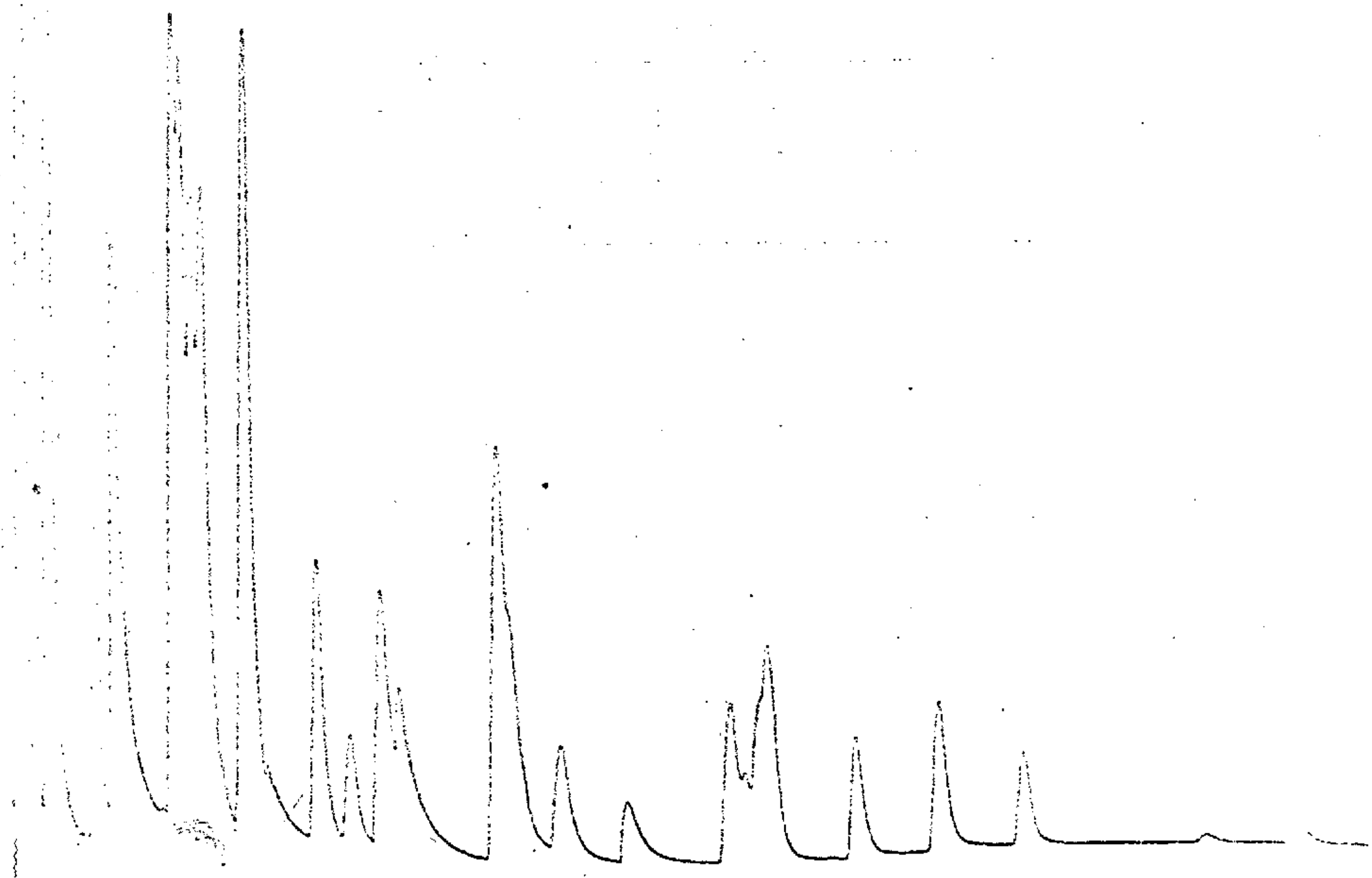
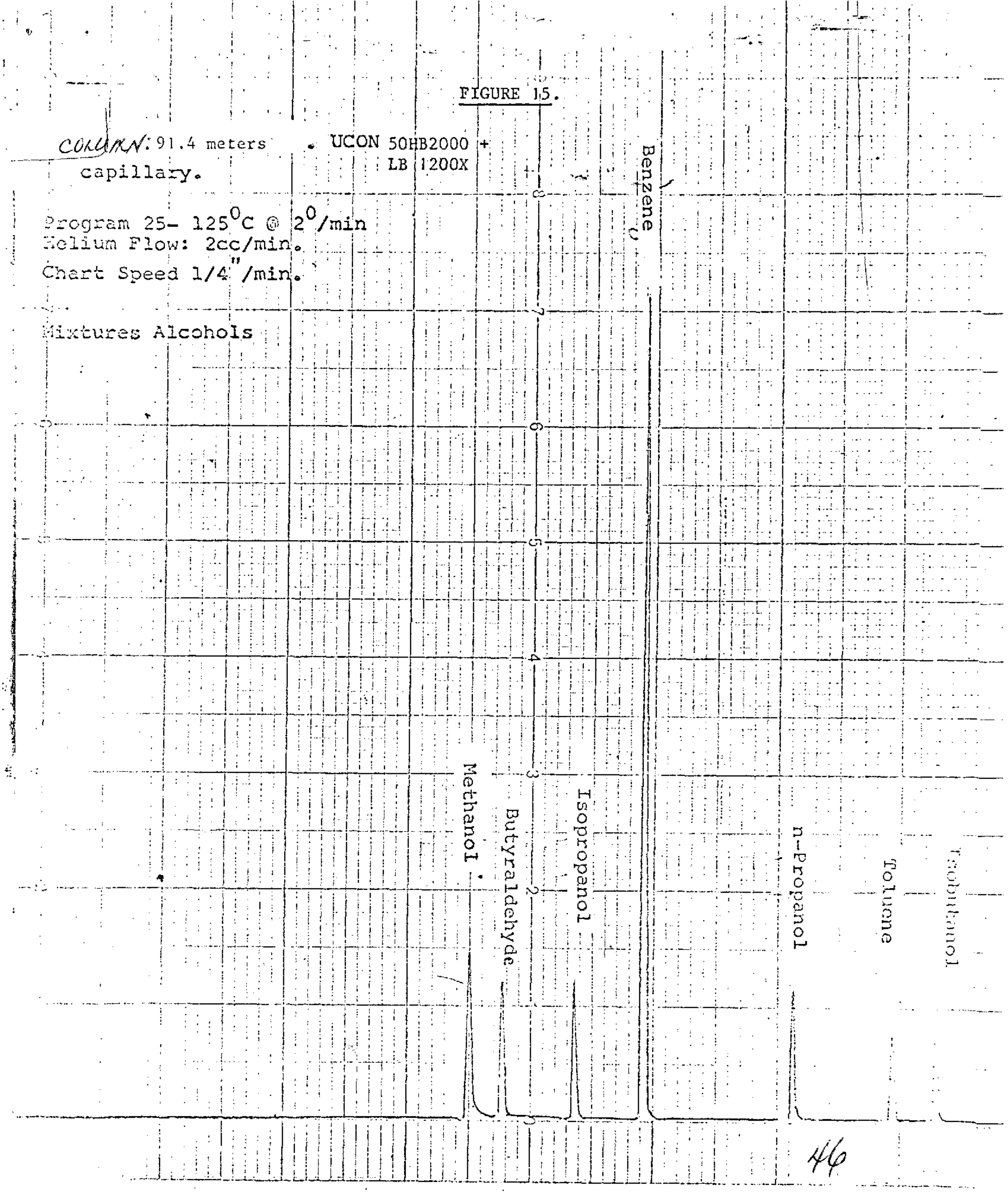


FIGURE 15.



COLUMN: 91.4 meters capillary. UCON 50HB2000 + LB 1200X

Program 25- 125^{0}C @ 2^0/min
Helium Flow: 2cc/min.
Chart Speed 1/4"/min.

Mixtures Alcohols

<u>FIGURE 16</u>

91.4m AN 600 capillary

Program @ 4°/min from 25°C to 130°C

Sample: Alcohols.

Helium flow rate: 5cc/min.

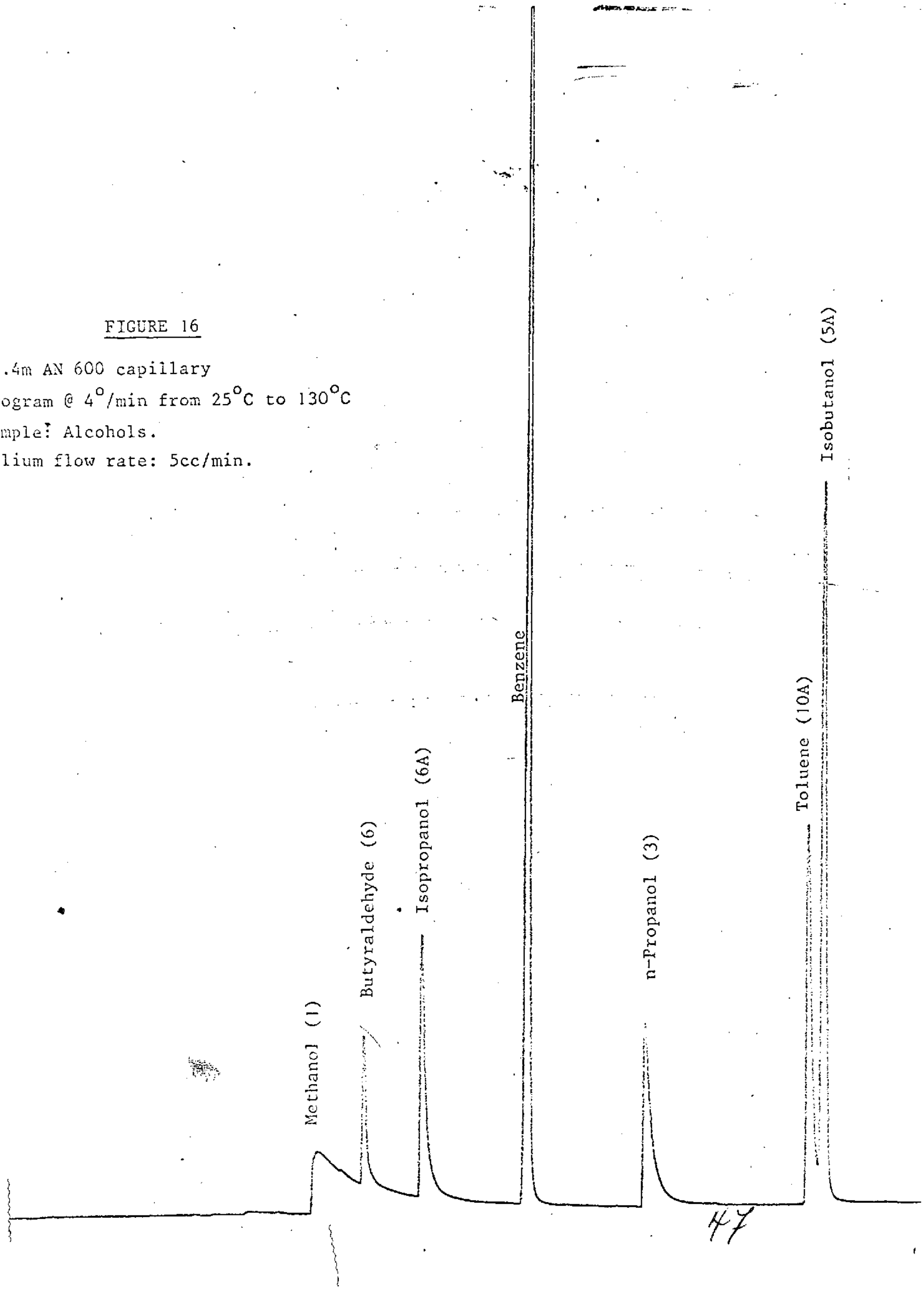
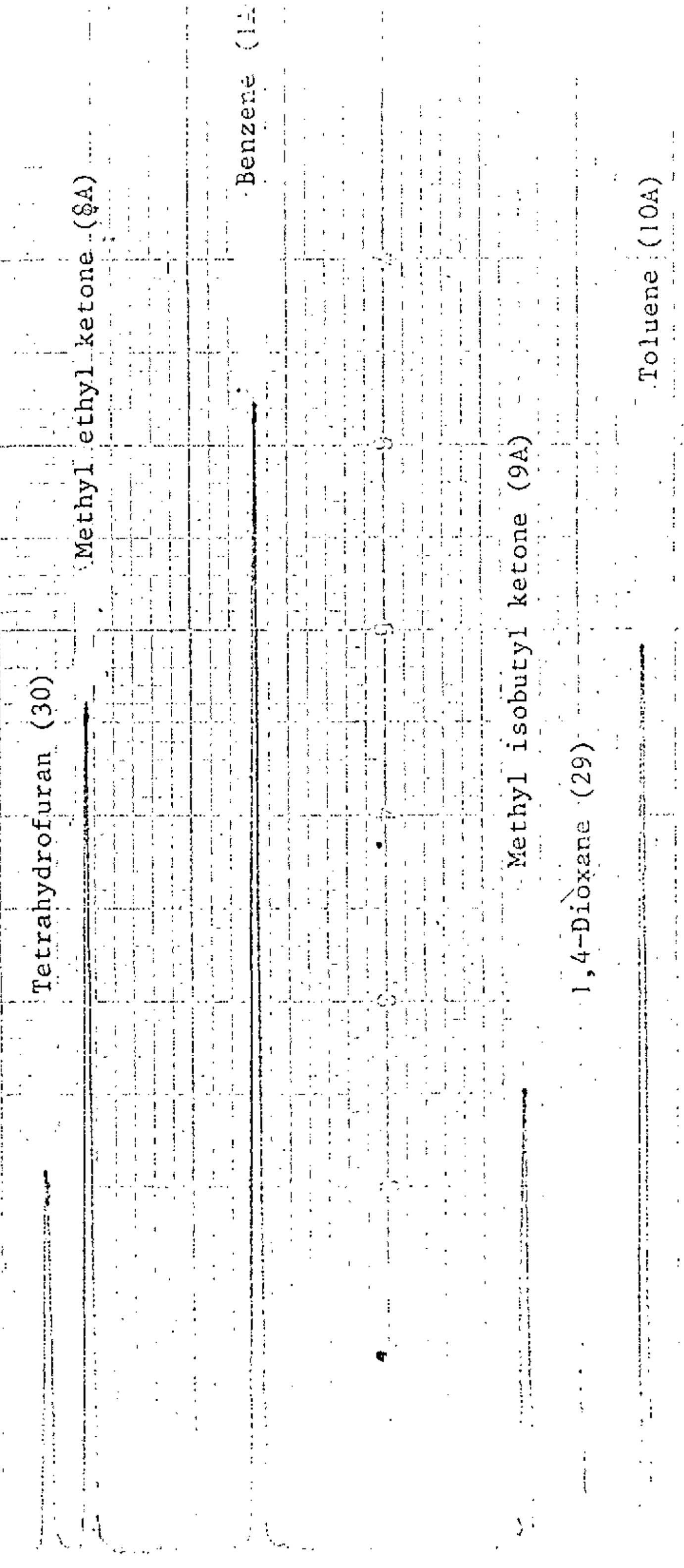


FIGURE 17

91.4 m Mixed Ucon column (C.7)
Isothermal for 6mins at 25°C then program
@ 4°/min to 120°C. Helium 4.5 cc/min.
Chart speed 1/4" / min.
Sample: Ketones.



HB

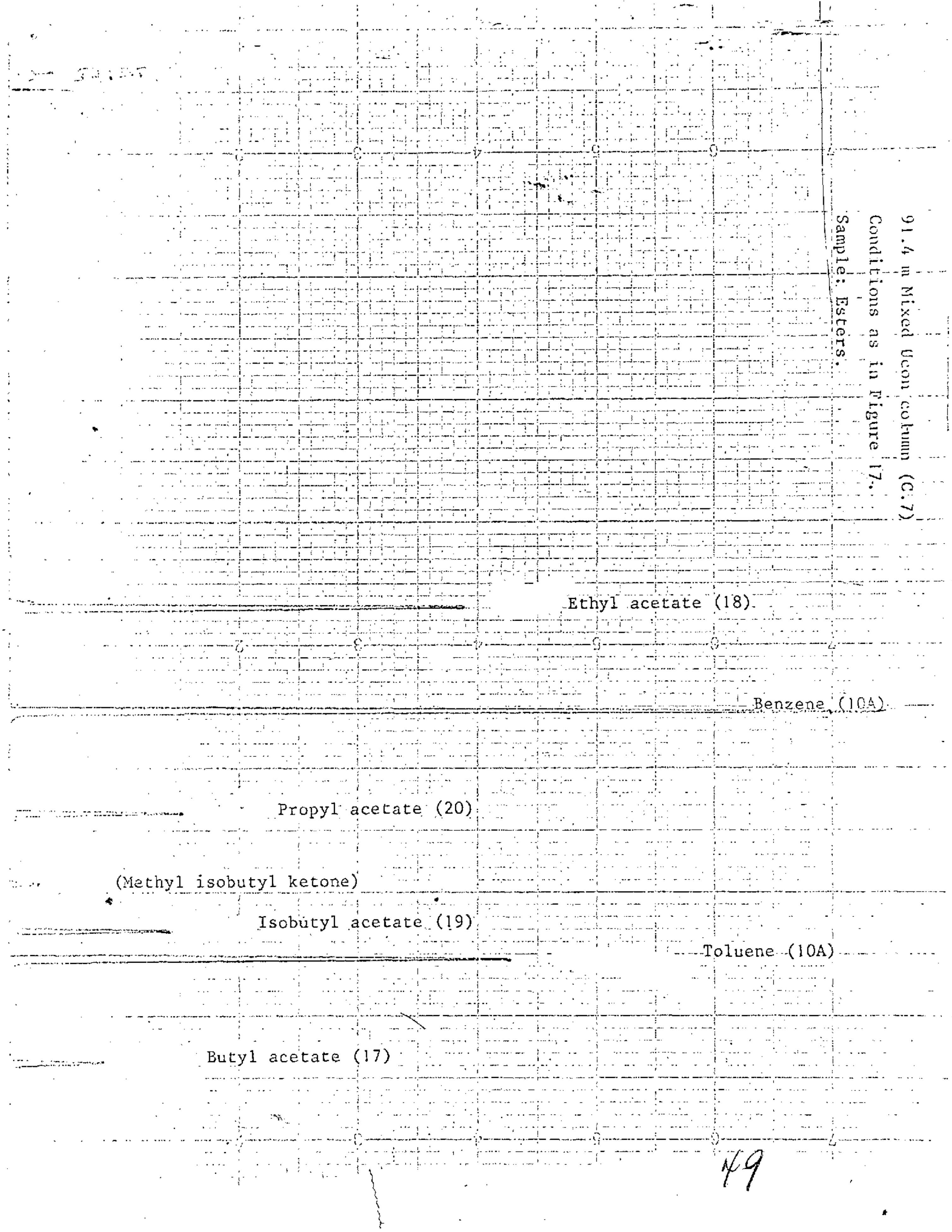


FIGURE 18

91.4 m Mixed Ucon column (C.7)

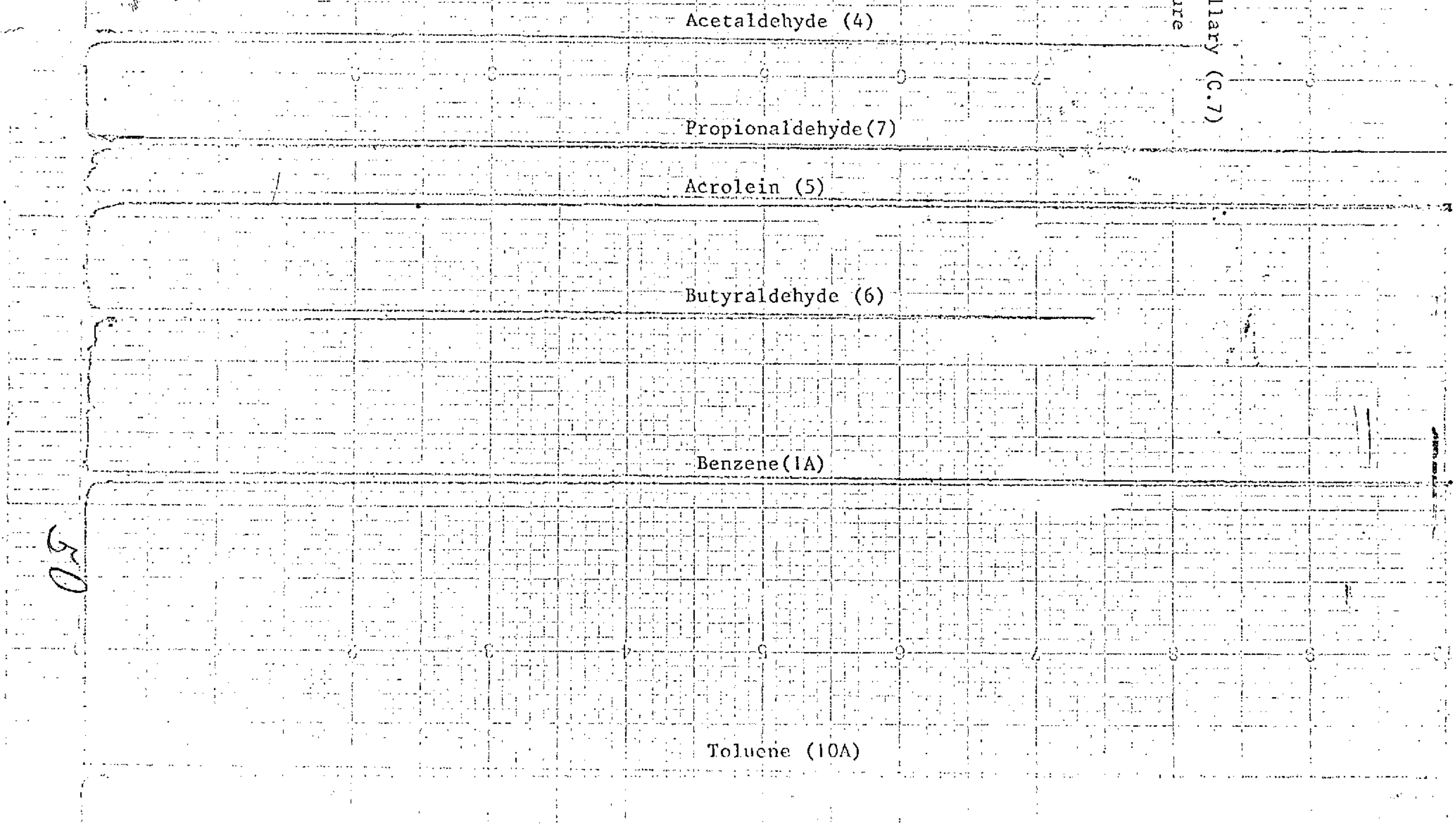
Conditions as in Figure 17.

Sample: Esters.

FIGURE 19

91.4 meter Ucon capillary (C.7) Conditions as in Figure 17.

Sample: Aldehydes.



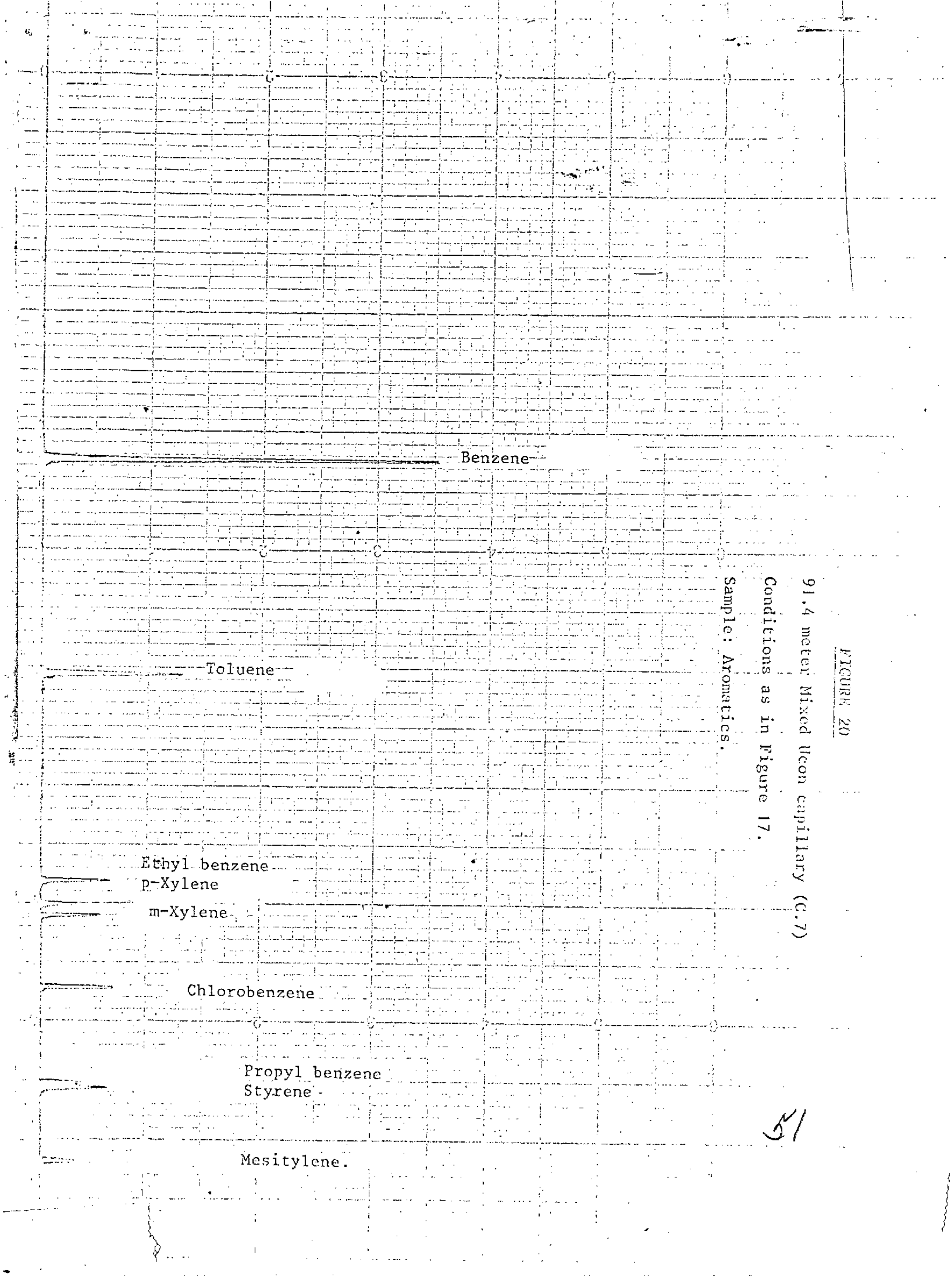


FIGURE 20

91.4 meter Mixed Ucon capillary (C.7)

Conditions as in Figure 17.

Sample: Aromatics.

FIGURE 21.

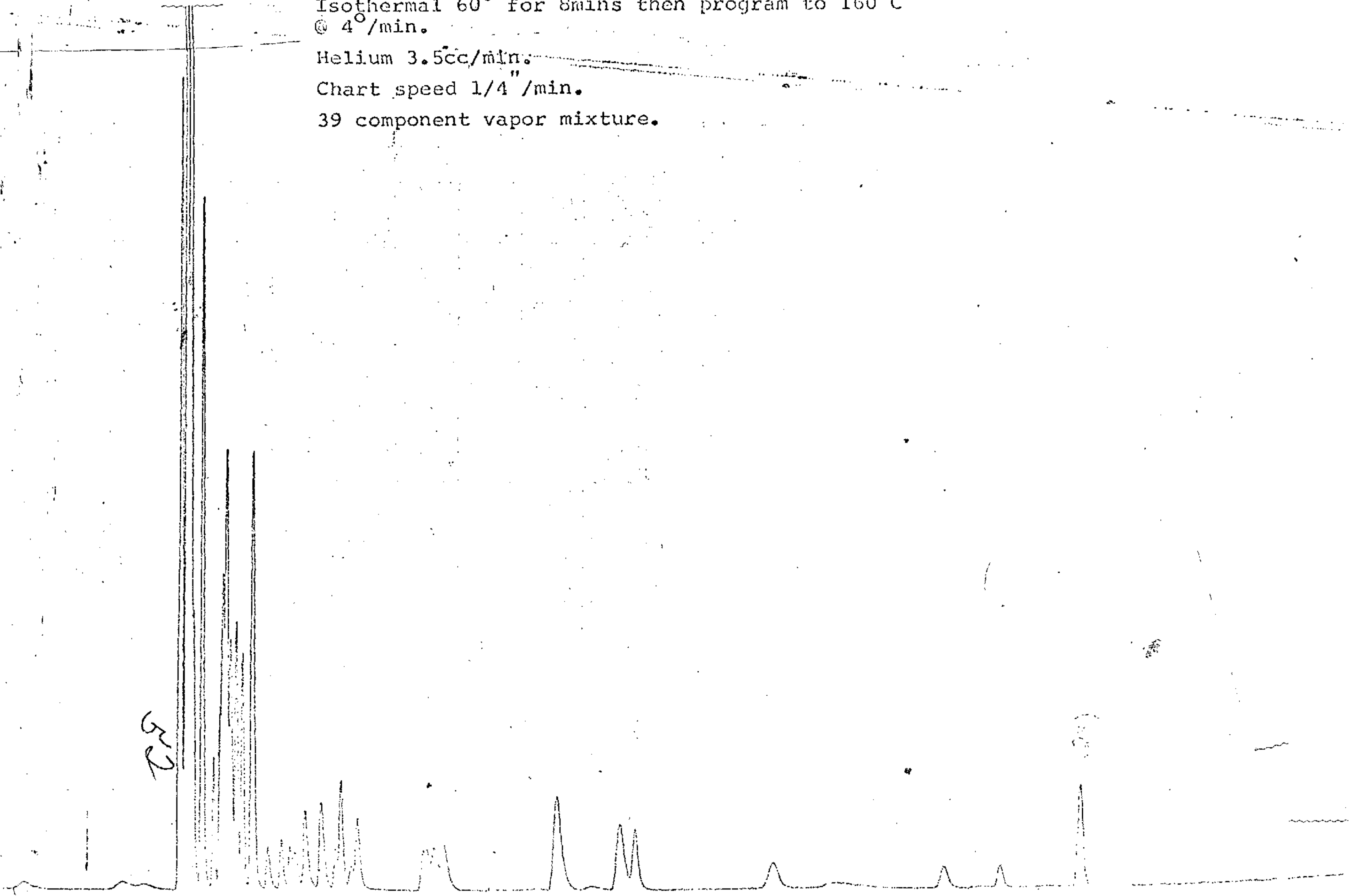
91.4 meter Carbowax 20M Capillary.

Isothermal 60° for 8mins then program to 160°C @ 4°/min.

Helium 3.5cc/min.

Chart speed 1/4"/min.

39 component vapor mixture.



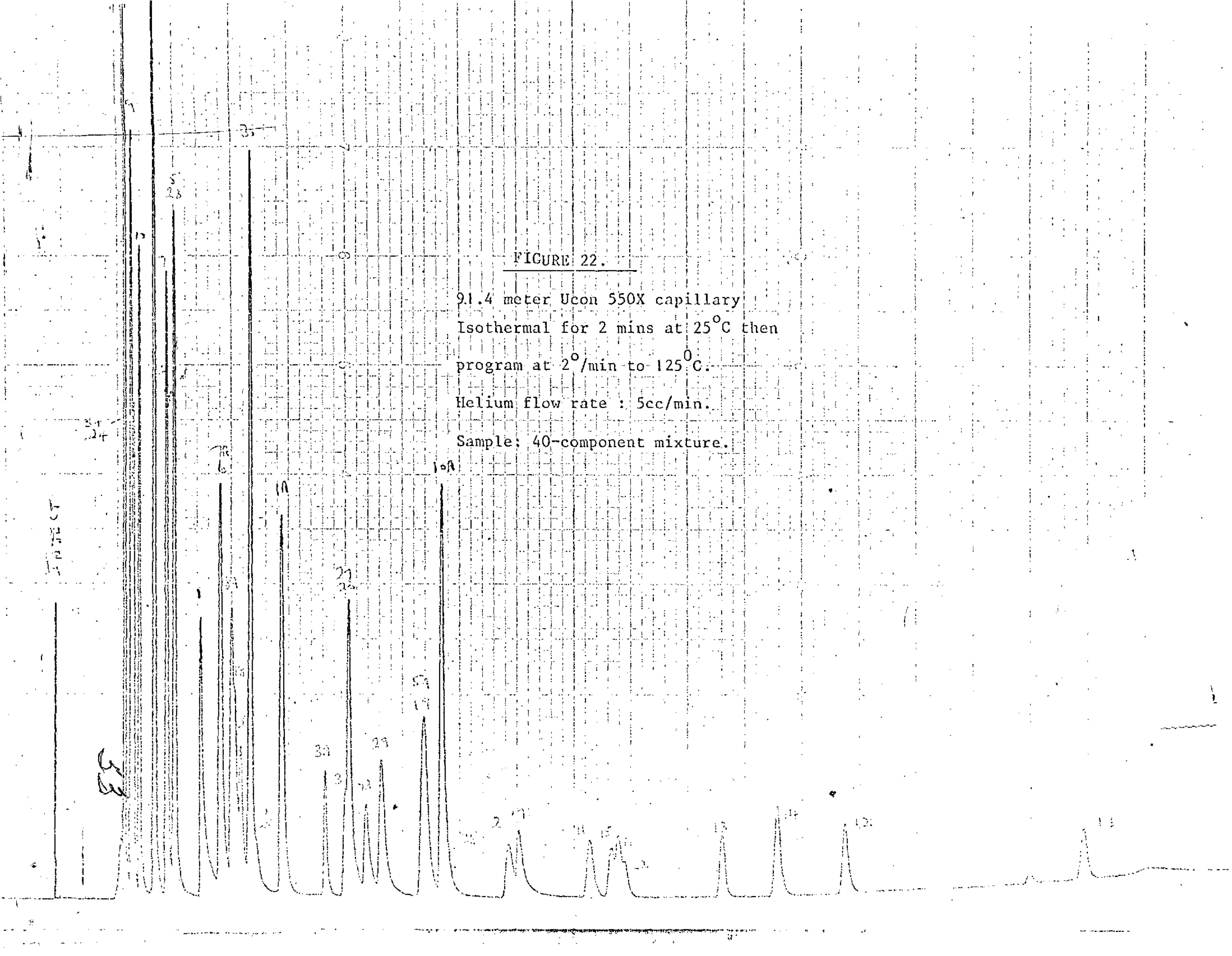


FIGURE 22.

91.4 meter Ucon 550X capillary

Isothermal for 2 mins at 25°C then

program at 2°/min to 125°C.

Helium flow rate : 5cc/min.

Sample: 40-component mixture.

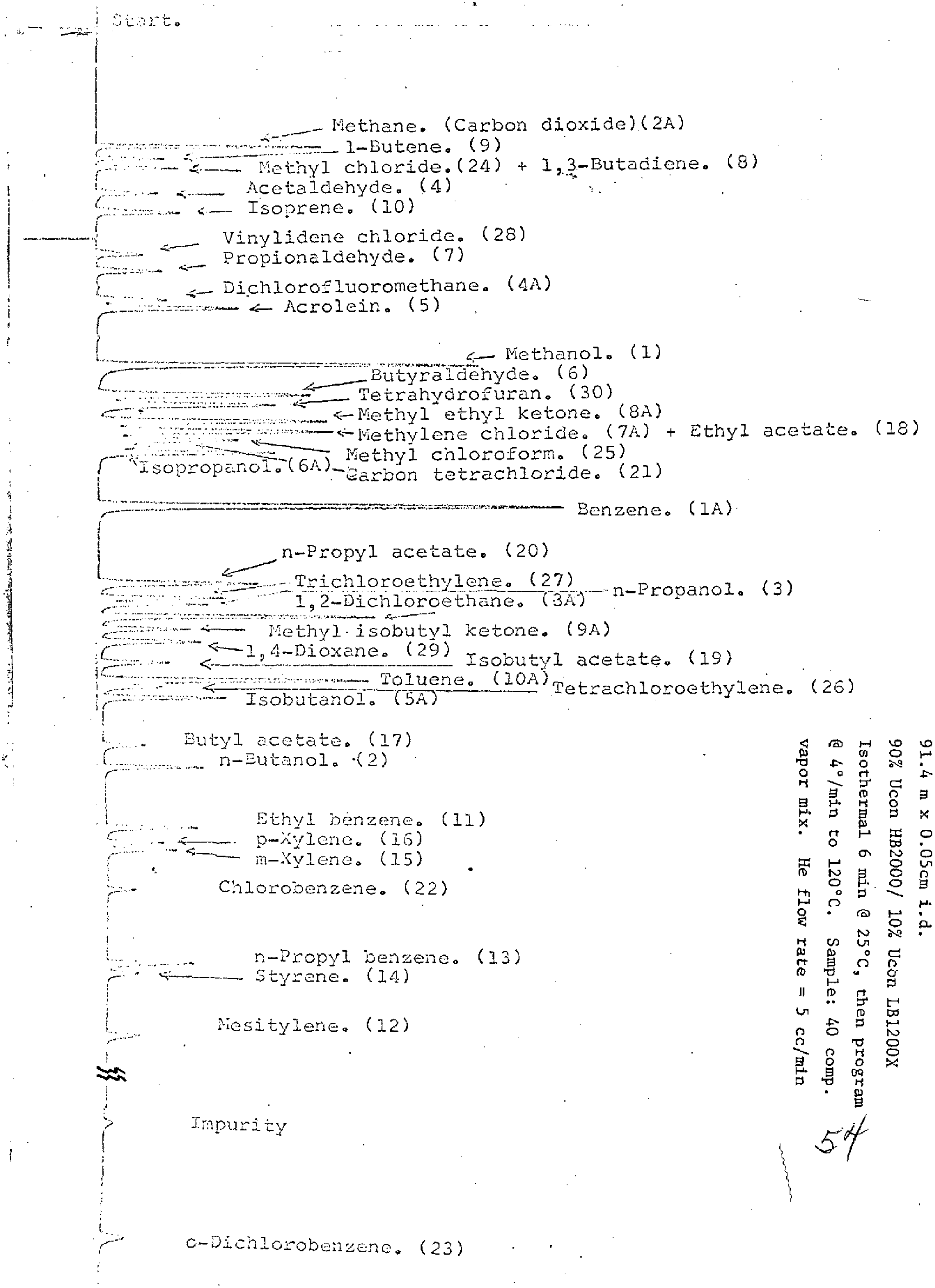


Figure 23

91.4 m x 0.05cm i.d.
90% Ucon HB2000/ 10% Ucon LB1200X
Isothermal 6 min @ 25°C, then program
@ 4°/min to 120°C. Sample: 40 comp.
vapor mix. He flow rate = 5 cc/min

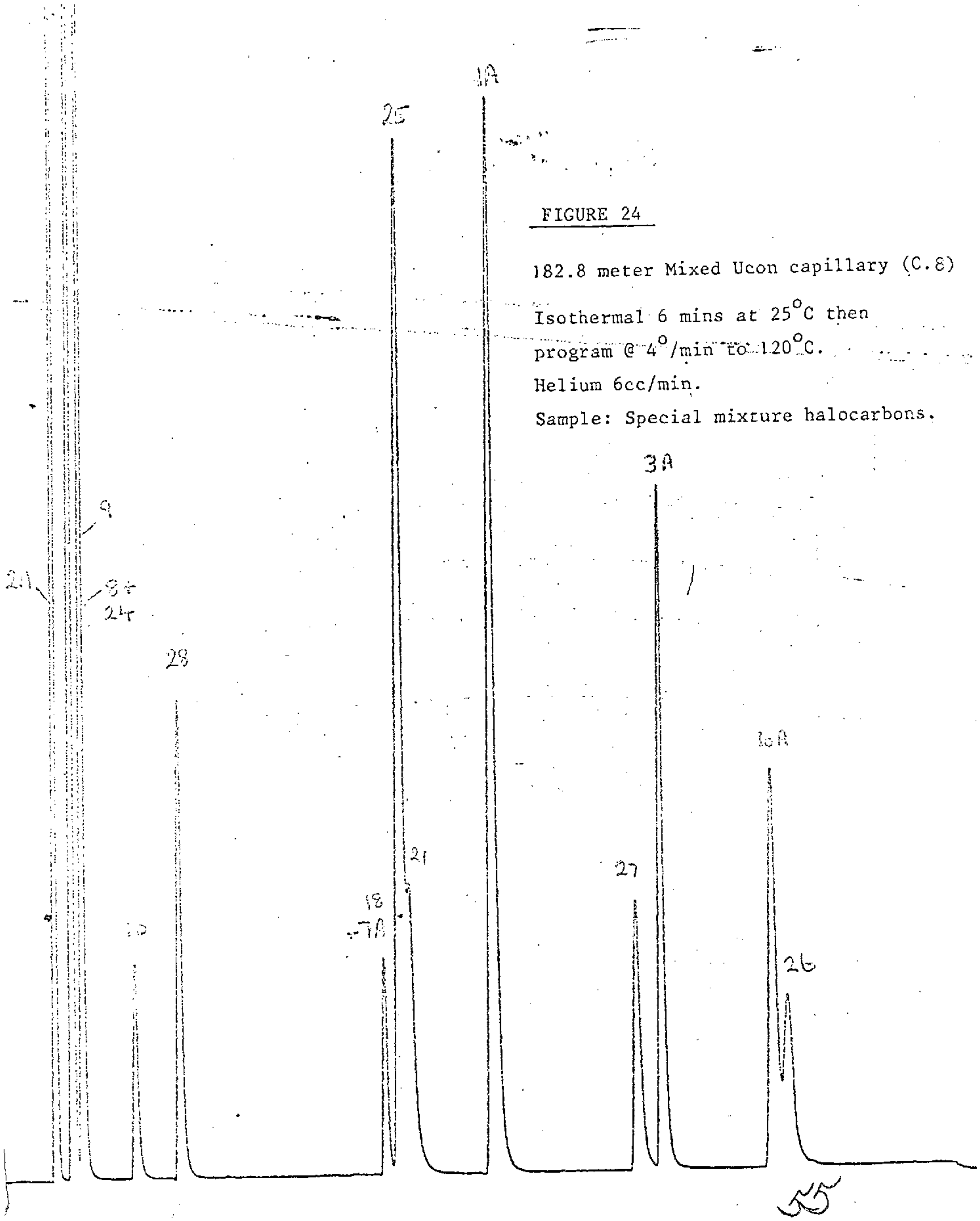


FIGURE 24

182.8 meter Mixed Ucon capillary (C.8)

Isothermal 6 mins at 25°C then
program @ 4°/min to 120°C.
Helium 6cc/min.
Sample: Special mixture halocarbons.

FIGURE 25.

91.4 meter capillary

85% Ucon 50HB2000 + 15% Ucon LB1200X.

Isothermal 70°C. Hydrogen flow rate 10cc/min.

Sample: 40-component vapor mixture. Chart speed 1/4"/min

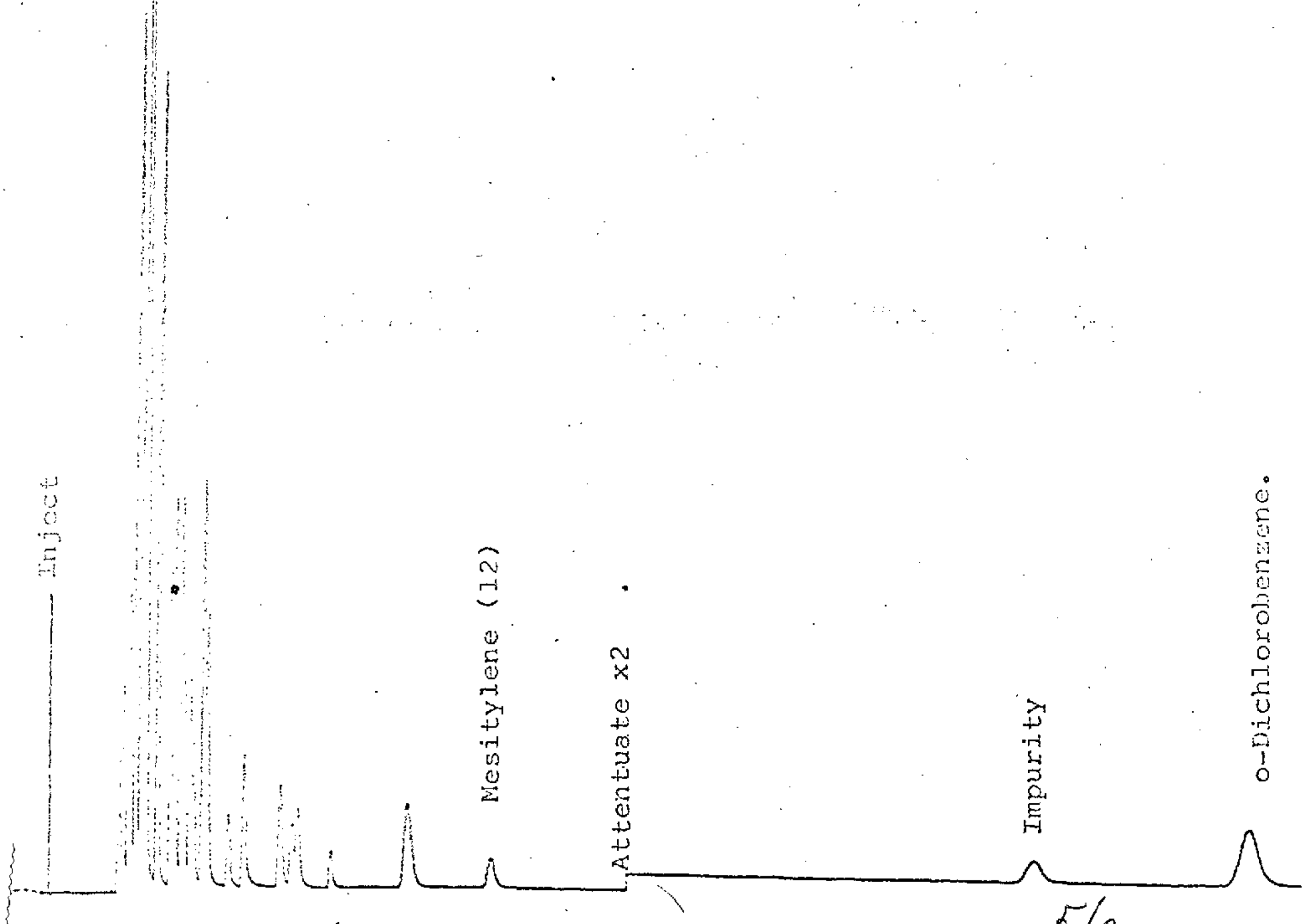
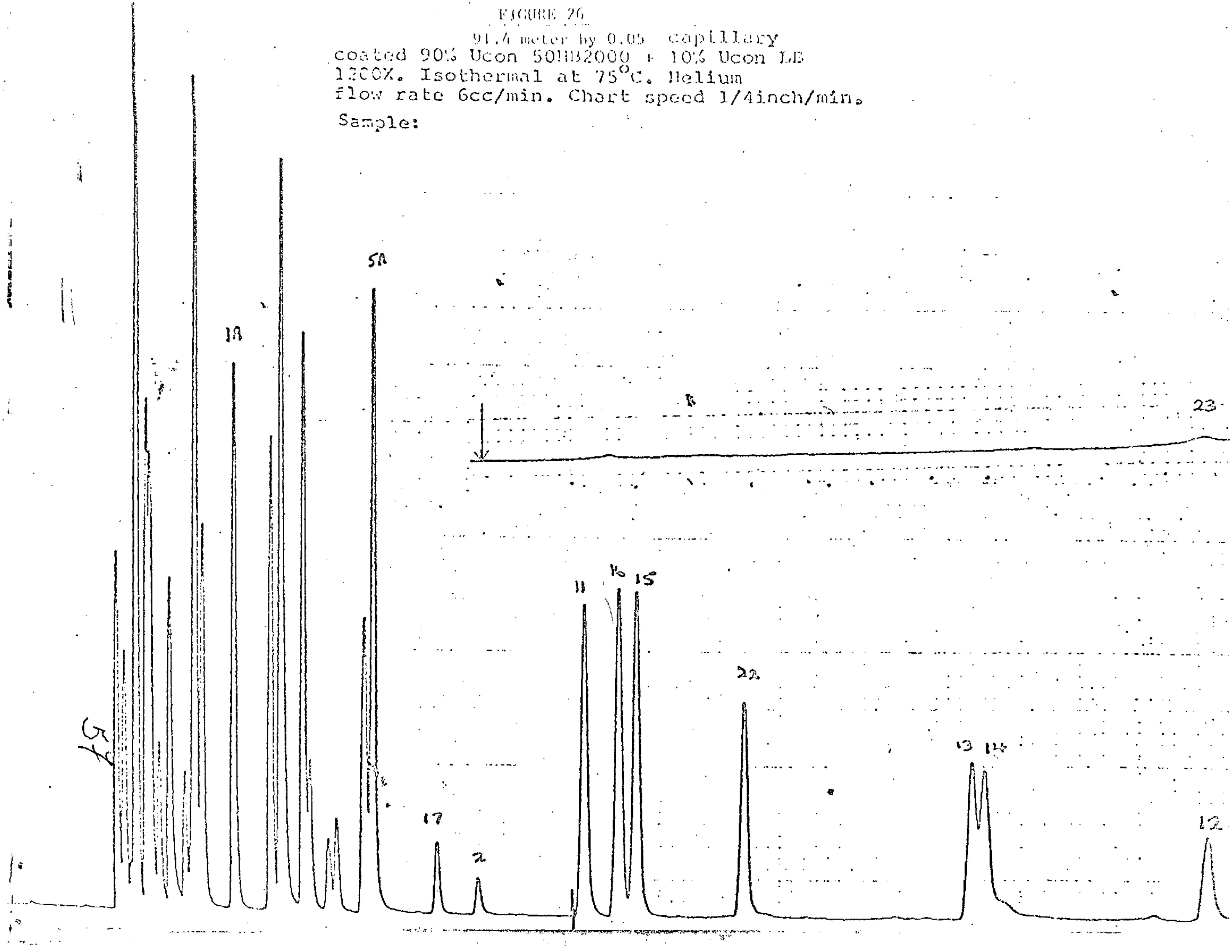


FIGURE 26

91.4 meter by 0.05 capillary coated 90% Ucon 50HB2000 + 10% Ucon LB 1200X. Isothermal at 75°C. Helium flow rate 6cc/min. Chart speed 1/4inch/min.

Sample:



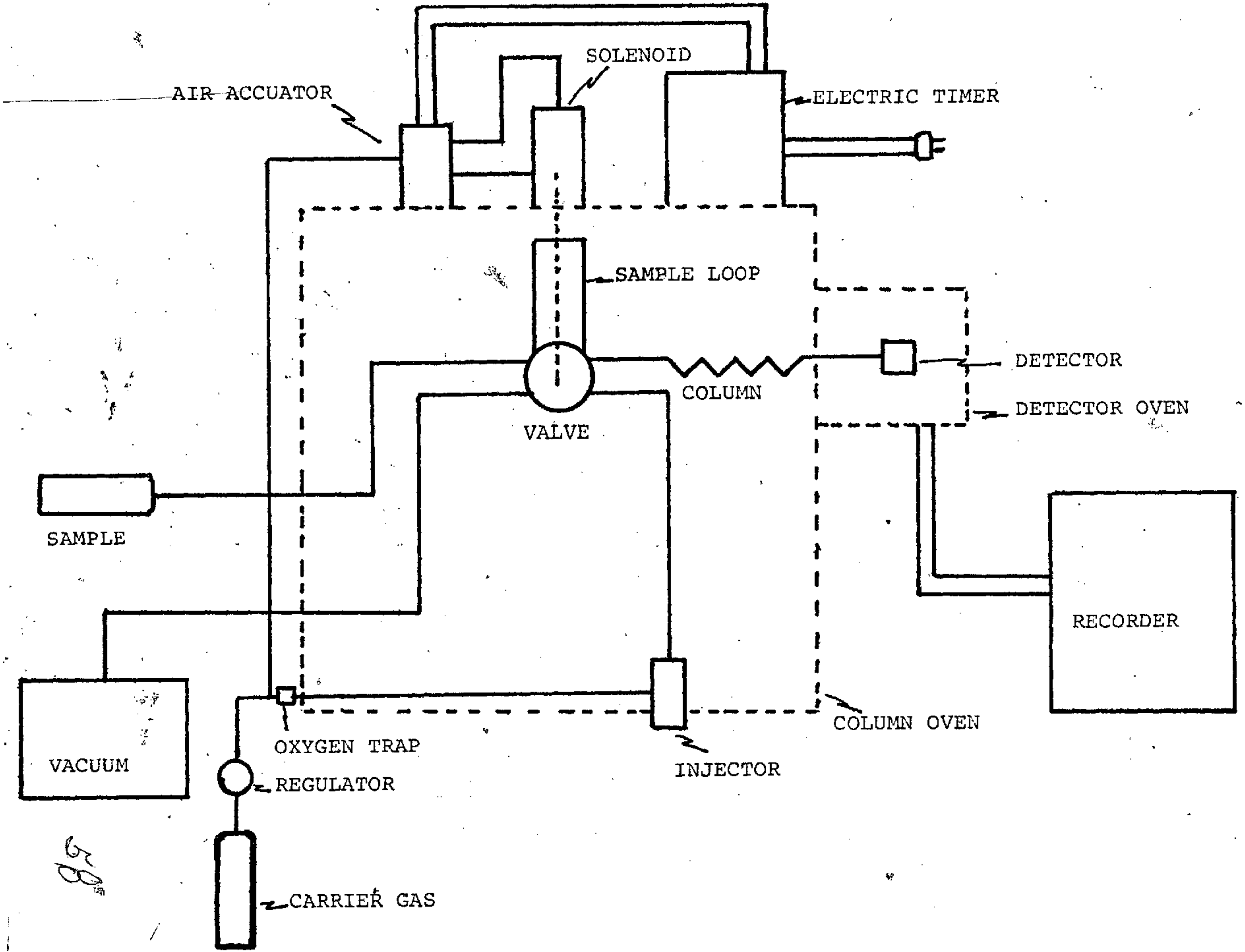
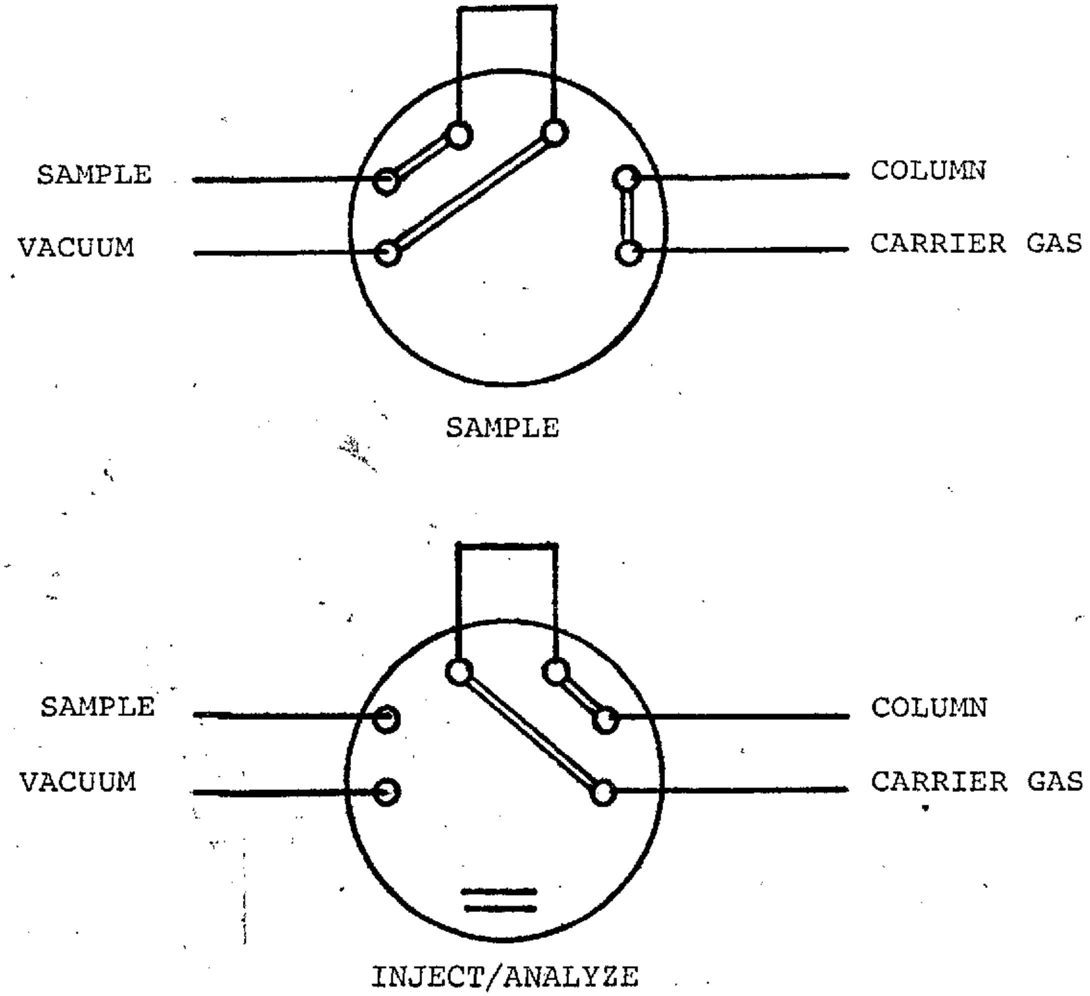


FIGURE 27.
SAMPLE TEST SYSTEM



SAMPLE VALVE CONFIGURATION

FIGURE 28.