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# The thermal, catalytic decomposition of sugar

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Thesis

**THE THERMAL, CATALYTIC DECOMPOSITION OF SUGAR**

by

**Herman Carl Kluge II**

UC 1963

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**Senior Thesis Submitted  
in Partial Fulfillment  
of the Requirements for Graduation**

**DEPARTMENT OF CHEMISTRY**

**UNION COLLEGE**

**MAY, 1963**



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THE THERMAL, CATALYTIC DECOMPOSITION OF SUGAR

by

Herman Carl Kluge II

A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science with a Major in Chemistry.

By Herman C. Kluge II

Approved by Prof. Schaefer

May 20, 1963



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Introduction

During the past year, an attempt was made to determine the products of a thermal decomposition of both glucose and fructose and also, the effects of certain catalysts upon this decomposition. From these data, an attempt was also made to devise a mechanism for this decomposition.

Historical

As early as 1919, the phenomenon of burning sugar in cigarette ash was noted by C. Thomas (9). In a short article on the subject, Thomas stated that he believed the catalytic action of ferric oxide in the ash caused the sugar to burn with a bluish flame.

In 1920, Dr. L. Brandt (2) tried without success to repeat Thomas's experiment using pure ferric oxide.

After extensive research and testing, J. Arvid Hedvall (6) published, in 1920, the most complete list to date of catalysts used to burn sugars. Hedvall classified these compounds in the following manner:

I Compounds which had no effect:

- A. oxides or hydroxides of weak bases
- B. Aluminum, iron, Nickel (filings)
- C. Nitric acid, acetic acid
- D.  $\text{CaF}_2$ ,  $\text{BaSO}_4$ ,  $(\text{NH}_3)_2\text{Co}_3$

(2)

II Catalysts which caused sugar to burn:

A. strong basic oxides and hydroxides

B.  $\text{CuO}$ ,  $\text{PbO}$ ,  $\text{Sb}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CoO}$ ,  $\text{Fe}_2\text{O}_3$  ( $\text{FeCl}_3 + \text{NaOH}$  at  $700^\circ \text{C}$ )

C. silver, copper, zinc, nickel (reduced), cobalt

III Catalysts which caused the sugar to burn leaving a dark residue:

A. halogens and free acids

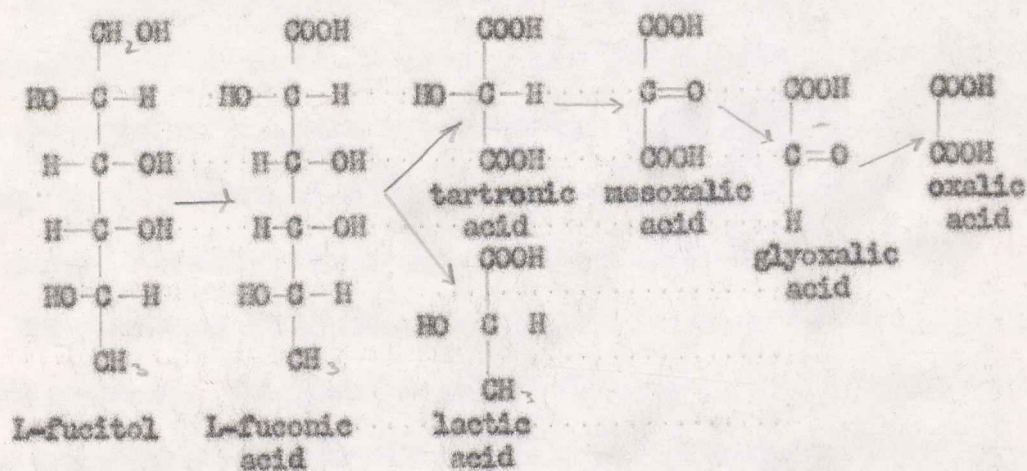
B. most salts

Then in 1925, G. Klein (7) attempted the first controlled reaction of sugars (both aldoses and ketoses) with different types of catalysts. Klein dissolved the sugars in pure distilled water and then distilled the mixture. Both type II and type III Hedvall catalysts were used. All examined pentoses and hexoses produced aldehydes, particularly formaldehyde, with small traces of organic acids.

More recently, Seiichi Okui (8) studied, specifically, the platinum catalytic oxidation of L-fucitol. The reactants were placed in a reaction vessel through which air was bubbled. At the end of the reaction, acetic acid was found in the air. The remarkable reducibility of the reacted solution caused him to believe that there might be intermediate aldehydes. Analysis of the products was made using paper chromatography. From these results, the following mechanism was proposed:



(3)



Last year, J. Williams (10) found that decomposition of sugar in the absence of air yielded low molecular weight acids and possible aldehydes. However, no mechanism was proposed. Acids would indicate an oxidation during the decomposition and thus, a possibility that Okui's reaction and Hedvall catalysts would prevail even in an inert atmosphere.



(b)

### Apparatus

All reactions were carried out in a helium atmosphere, to eliminate the possibility of oxidation of the sugar by the air. A silicone oil bath was employed to assure even heating. A variac supplied a variable voltage to a filament of coiled nichrome wire. All tubing and glassware was pyrex. The temperatures recorded were those of the oil bath.

The apparatus (diagram I) was designed for intermittent gas sampling of the products. The instrument used for analysis was a Perkin-Elmer model 154-D vapor phase refractometer, with a 5.0c.c. sampling attachment. The various products were separated as a function of their thermal conductivities using an R column (U con polyglycol LB-550-K). This is a moderately polar general purpose column for moderate temperatures (Up to 200°C). The results were plotted on graph paper by an automatic recorder. For all graphs, one unit of horizontal deflection is equal to a time of twelve seconds. Thus, from the number of deflections, it would be possible to measure the retention time of each peak.

Helium was chosen as the gas to supply the inert atmosphere since this was also the carrier gas of the V.P.C.

(5)

Experimental Results

data:

decomposition				
	temperature, ° C			
run	column	melting	bubbling	sampling
1	100	140	170	157, 160, 170, 180, 190, 200
2	100	114	114	107, 118, 149, 150, 166, 184, 192
5	100	160	170	146, 160, 170, 176, 178, 182, 189, 212

distillation				
	temperature, ° C			
run	melting	bubbling	boiling	color
3	211	221	230-274	-----
4A	---	---	100-110	colorless
4B	---	---	110-120	yellow-brown

Comments on Experimental Results:

Run #1 - g. glucose

The sample began to condense and reflux in the trap and flask at 190° C. At 200° C., the substance in the flask turned to black, carbon residue. This graph (1A) revealed only one major peak which to be water.

A certain amount of distillate was caught in the trap. This was analyzed directly by the V.P.C. (graph 1B). on a relatively low



(6)

sensitivity (x128), the major peak appeared again only to be water. However, the distilled product was yellow-green in color and acidic to litmus.

Run #2 - 10 g. glucose 1 g.  $\text{HgCl}_2$  (type III Hedvall catalyst)

The same black residue formed at  $118^\circ\text{C}$ . By  $195^\circ\text{C}$ ., the reaction was complete. The catalyst had a marked effect upon the temperature at which the reaction started. It should also be noted that the carbon residue formed almost immediately upon melting.

The graph of this reaction (graph 2A) is very similar to graph 1A. That is, only one major peak, water, is present. However, the water peak is much larger in graph 2A than in graph 1A. Again the trapped distillate was analyzed (graph 2B) and found to contain the same water peak. There were a number of very small peaks which would have been more clearly discernible at a higher sensitivity.

Run #3 - distillation of 40 g. of glucose.

At this point, a distillation in inert atmosphere was performed. The objective was to obtain larger amounts of the liquid distillate. The apparatus shown in diagram 2 was used for this and all other distillations.



(7)

Run #1 - distillation.

A boiling point was run on the yellow-brown liquid distillate, and separated into two fractions. ten ul. of each fraction was run directly in the V.P.C. These two runs were compared with runs of acetic and butyric acids and water.

The major peaks of fractions, 4A and 4B (see data) appear on graphs 4A and 4B. These peaks agreed completely with that of water (graph 4C). The peaks of either acetic or butyric acids (graph 4D and 4E, respectively) did not have the same time retention as the minor peak of 4B. It is possible that the relatively large water peak displaced the minor peak, still leaving the possibility that this peak was either acetic or butyric acid.

Run #5 - 10 g. fructose.

The mercuric chloride catalyst did lower the temperature of the decomposition. However, no other information could be gathered with respect to products and mechanism. A number of very minor peaks had been noticed in this and preceeding runs. Therefore, if there were any low molecular weight, volatile acids or carbonyls present in the product, they were in very small amounts. It was decided to try a greater sensitivity and a different sugar, fructose, in a decomposition with intermittent gas sampling (diagram 1).

At first, the only peak observed was water (graph 5A). However,



(8)

the size of this peak decreased with increasing time and temperature. At a sampling temperature of 182°C., the water peak was approximately as large on x8 sensitivity as it was at the beginning on x128 also, a wide, diffuse band appeared at 182°C. At succeeding sampling temperatures, this peak decreased in size until at 212°C., it was visible only on x1 sensitivity.

The same yellow-green distillate was found in the trap. A V.P.C. was run on the distillate. A number of peaks were found using the higher sensitivities, but not the wide, diffuse band (graph 5B). As in the case of all liquid samples, only ten microliters of distillate was analyzed. This would be a smaller amount of product analyzed than used for gas samples. Thus the larger amount of carbonyl produced by the decomposition could have a greater probability of reacting with the polyglycol present in the R column than the smaller amount of easily vaporized carbonyl in the liquid sample. Accepting this, it is possible to believe that the wide diffuse band was due to carbonyls produced by the decomposition, and the peaks in graph 5B are the acids and/or carbonyls in smaller amounts.

It was evident that acids were present due to the reaction with litmus. However, it was impossible to conclude whether aldehydes or ketones or both were present as products. Therefore, a qualitative organic analysis was attempted. In order to have enough product for this and any possible tests in the future, sixty grams of fructose

(9)

was distilled in the same manner as Run #3. Three fractions totaling approximately eight ml. of product were obtained.

Using the procedure of Shriner, Fuson, and Curtin 2,4 dinitro-phenylhydrazones of the carbonyls were prepared using 2,4 dinitro-phenylhydrazine solution (3). A melting point of the solid derivative was in a range from 115-116°C., and therefore inconclusive as to what carbonyls were present. The possibilities melting in the above range are:

- (1) formaldehyde
- (2) acetaldehyde
- (3) acetone
- (4) methyl ethyl ketone

If either of the above ketones were present, it would appear that the placement of the keto group in the fructose has some sort of effect on the reaction. The bond energy of the C=O bond is 173 k cal/mole while the bond energies of the C-C and C-O bond are 80 k cal/mole and 79 k cal/mole respectively. Thus, there is a greater probability that the ladder bonds broke during decomposition, but not the former.

Since fructose is a hexose, and because of the position of the keto-group it seemed plausible that any of the following acids might be present as products:



(10)

- (1) acetic acid
- (2) propionic acid
- (3) butyric acid
- (4) valeric acid

It was felt that paper chromatography might substantiate or eliminate some or all of the possibilities. For the best possible results, it was decided that twenty-four hour, two dimensional chromatograms should be run on the products of the previous fructose distillation and the glucose distillation. Chromatograms of the unknowns could be compared with chromatograms of the possible acids and carbonyls by their relative rates of flow. The procedure was carried out in a large glass tank with a plate glass top sealed with stop-cock grease (diagram 3). Dowex #1 chromatogram paper was cut into strips 18 x 56 cm. and suspended by metal clamps inside the tank, the lower end of the paper being placed in the solvent tray.

The following paper preparations, solvents, and developers were used in order to analyze acids as their ammonium salts and carbonyls as their 2,4 dinitrophenylhydrazones (1):

#### I acid chromatograms

##### A. preparation of paper

(11)

1. paper strips were washed once with
  - a. 2N acetic acid
  - b. water
  - c. 10N ammonium hydroxide
2. paper strips were allowed to dry
- B. solvent in 1:1 volume-volume ratio
  1. n-butanol
  2. 15 N ammonium hydroxide
- C. developer

40 mg. of bromocresol green in 100 ml. of water made alkaline with dilute sodium hydroxide

## II carbonyl chromatograms

- A. preparation of paper
  1. paper strips were washed once with
    - a. 1 percent oxalic acid
    - b. water
  2. paper strips were allowed to dry
- B. solvent in 1:1 volume-volume ratio
  1. 95 percent ethanol
  2. petroleum ether
- C. developer

150 mg. of 2,4 dinitrophenylhydrazine in 20 ml. of concentrated hydrochloric acid with enough water to make 100 ml.



At the end of the twenty-four hour period, the Chromatograms were sprayed with the respective developers using the spray bottle illustrated in diagram 3. The acid and carbonyl chromatograms are shown as graphs 6A and 6B respectively. According to these chromatograms, the rates of flow seemed to be paired. That is, the groupings, acetone-methyl ethyl ketone, acetaldehyde-formaldehyde, acetic propionic acids, and butyric-valeric acids were very close together. Because of this, it was impossible to tell exactly which one, if not both, of each group of compounds were present in the unknown.

There were eight possible compounds present in the decomposition mixture. It was decided that a catalog of possible knowns should be made using the vapor phase. These knowns could be compared with the unknown distillate of the last fructose distillation. Because of the small amounts of product present in relation to the large amounts of water, the highest possible sensitivity was used. The runs of known carbonyls appear compositely in graph 7A. The runs of water and known acids, in the same manner, appear in graph 7B.

Then, a V.P.C. was run on each of three fractions containing the fructose distillate (graphs 8A,B,C respectively). Referring to the known graphs 7A and 7B, the following products appeared to be present.



(13)

- (1) water
- (2) formic acid
- (3) formaldehyde
- (4) propionic acid
- (5) butyric acid
- (6) valeric acid

Composing the relative amounts of products in the three successive fractions, it appears that as the distillation proceeded, the amount of formaldehyde, butyric acid, propionic acid, and valeric acid increased markedly. It must be noted that the intermediate acid, acetic acid did not show in the chromatograph. It is possible that the large amount of water present masked its peak.

It was next decided to determine the products of a catalyzed reaction. Once again, mercuric chloride (type III Redvall catalyst) was employed, but this time using fructose. 40 grams of fructose were mixed with 10 grains of mercuric chloride. The mixture was distilled using the apparatus of diagram 2. This distillate was then run through the V.P.C. The results are shown in graph 9. This graph is very similar to graph 8A. The same products were present and in approximately the same proportion. Again, it is possible that the large water peak masked the acetic acid peak. It must be noted also that this distillate was not fractionated as was the fructose distillate. That is, graph 9 is an all-over picture of the products present.



(14)

The solution did not have the characteristic smell of the previous distillate but that of hydrogen chloride. Adding a small amount of silver nitrate produced a white precipitate which was believed to be silver chloride. From this, it was supposed that chloride ions were present in the distillate. This would indicate that the mercuric chloride was reduced to chloride ions, and possibly free mercury might be left in the reaction flask.

Next, a distillation of fructose was run using the type II Hedvall catalyst, powdered zinc. 40 grams of fructose was mixed thoroughly with 5 grams of powdered zinc and distilled using the apparatus of diagram 2. Immediately after the distillation, the V.P.C. appearing in graph 10A was run. As usual, the largest product was water. A certain amount of formic acid, butyric acid, and propionic acid were also present. A very small peak showed a displacement equal to that of acetone. Also, two small bumps, very close together, which in reality could be one product, were noted.

Approximately two days later, the same distillate was run again on the V.P.C. There was a marked change in the shape of the curve. The amount of water had been halved. A small increase in the amount of acetone was noted. Also, there was evidence of the presence of formaldehyde with a decrease in formic acid. The amount of propionic acid had decreased with the development of a peak of equal size near by, where there had been two small bumps two days previously, only one remained. It seemed that acetone was now present. It was decided



(15)

that the two peaks of the previous graph, 10A, were acetaldehyde and acetic acid displaced by the large amount of water present which had disrupted the entire slope of that particular graph. It should be noted from graphs 7A and 7B that this acid and carbonyl have about equal retention time. This would indicate that it was the acetaldehyde had been converted to acetone and that it was the acetic acid which had decreased.

It was noted that the residue of the flask was a brittle, gray substance which melted between  $26^{\circ}$  and  $30^{\circ}$  C. Upon melting particles of unreacted zinc were noted. This substance would not dissolve in water, alcohol, ether, or concentrated sulfuric acid. This would leave the possibility that the compound might be a cyclic ring.

Mechanism of Reaction

In general, from the analysis of products, it appears that the keto-hexose, fructose decomposes to products containing one to five carbon atoms. Also, the presence of acids would indicate that an oxidation of the alcoholic sugar groupings also occurs.

Still generalizing, it seems possible, that as time progressed, the formic acid was reduced, producing formaldehyde. Slight evidence for acetic acid was found only in the last run. However, acetaldehyde in a small amount was also perceived in this run. This would be slight evidence that the acetic acid also was reduced to acetaldehyde. It could be further possible that the acetone noted was produced either by the oxidation of the acetaldehyde or the incomplete reduction of the acetic acid.

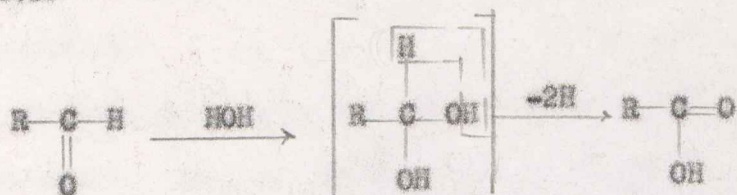
For the pure fructose and zinc catalyzed fructose decompositions, the amounts of butyric and valeric acids increased with increasing time but not to the extent that the propionic acid did. This would indicate that the fructose molecule tends to break near the keto group. It is possible that the sugar molecule usually breaks in the middle to form propionic acid and acetone, leaving the C O bond intact due to its relatively high bond energy as discussed previously.



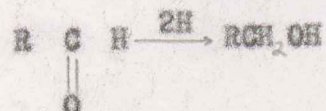
(17)

It should be remembered that very large amounts of water were found in the products of all decomposition. This would indicate a condensation accompanied by repeating oxidation and reduction.

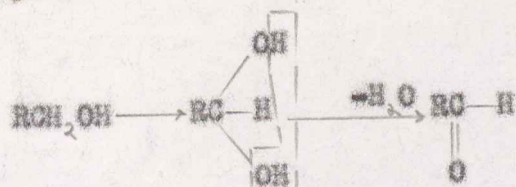
Aldehydes may be oxidized to their respective acids when the reaction proceeds through the transient formation of an unstable hydrate:



Aldehydes may also be reduced to their respective alcohols:



If, in an alcohol, one of the hydrogens attached to the already oxidized carbon were to become hydroxylated, the product would be an unstable gemdiol and would lose water to form the respective aldehyde:



This series of reactions (h) could be applied to the decomposition of sugars. When sugar itself is heated, water of conformation is given off. The higher temperatures decompose the sugar to smaller

products. The alcoholic linkage could be condensed to the aldehyde. The aldehyde reacts with the water of conformation or the water of condensation to produce acids or reduced to primary alcohols which again produce aldehydes in a continuous reaction. This would intimate that the presence of ketones is characteristic of keto-hexose decomposition and therefore should not be present in aldo-hexose decomposition.

It seems that catalysts in general do lower the decomposition temperature. However, it appears that the catalysts do not cause a change in the overall rate due to the fact that in each case studied, the catalysts entered into the reaction, forming final products of its own.



Suggestions for Further Work

Considerably more work should be done in this field. It should be possible to find aldehydes of all the respective acids that were separated. And, if the theory of reaction is correct, alcohols should also be present unless this step in the probable mechanism is too fast to be analyzed.

Intermittent gas sampling was found to be of little use because some of the gases condensed before they reached the sampler. Analysis is easiest when the sugar is distilled. For best results, the distillate should be kept out of contact with the air, since auto oxidation will continue even after the reaction returns to room temperature.

Further reactions should be carried on a large scale in order to obtain larger amounts of products. Perhaps then the balance of the water could be eliminated by drying. Also, in some manner, a thermometer should be placed in the decomposition flask to find out exactly the temperature at which the distillation begins.

Considerably more work should be done using glucose. Then, since sucrose is derived from glucose and fructose, this sugar should be studied.

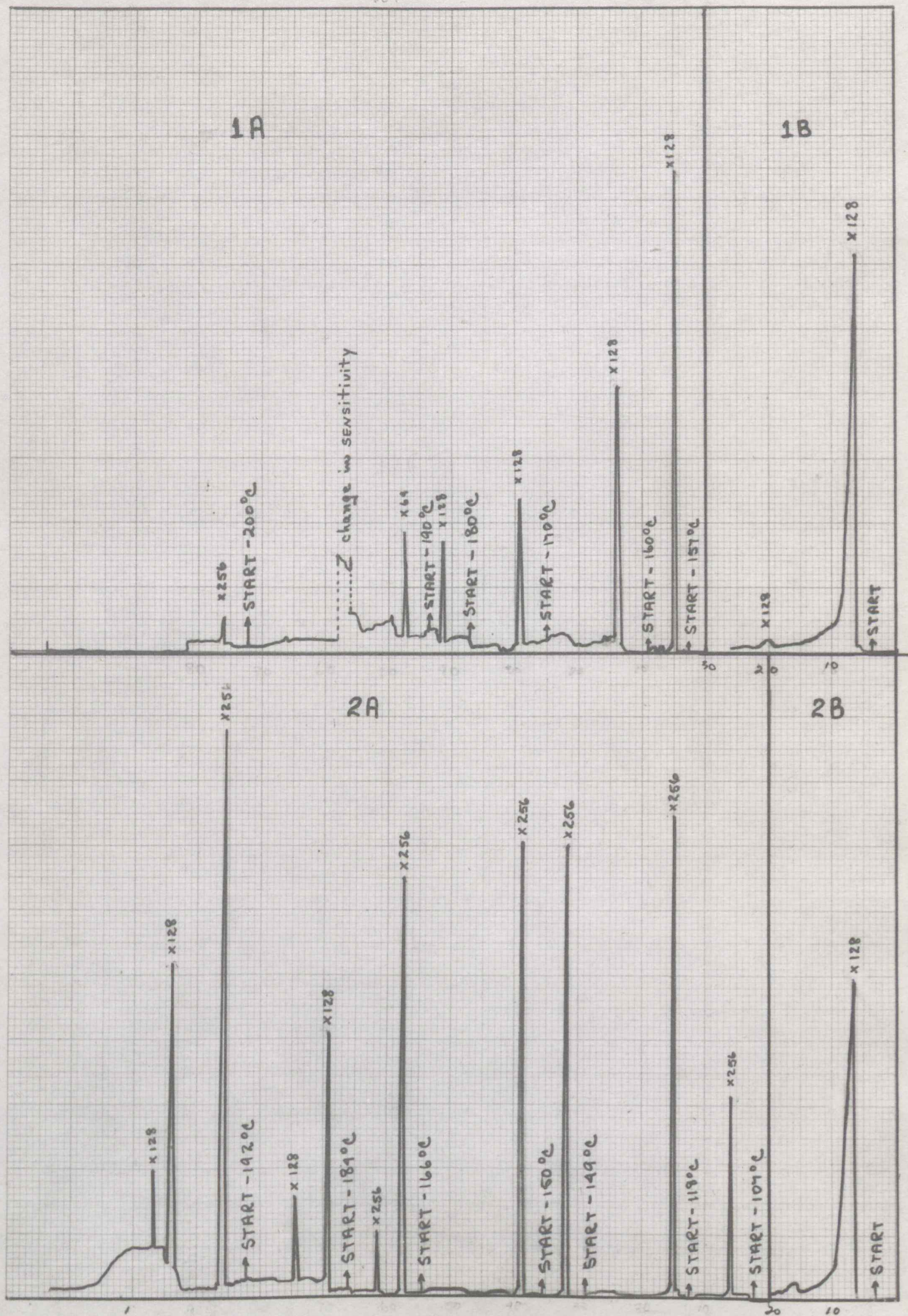
More of both Hedvall type I and type II catalysts should be studied. It should prove worthwhile to study the action of the catalyst when placed above the sugar, in the midst of the decomposition vapor. The transition catalysts should be studied in detail, especially those

(20)

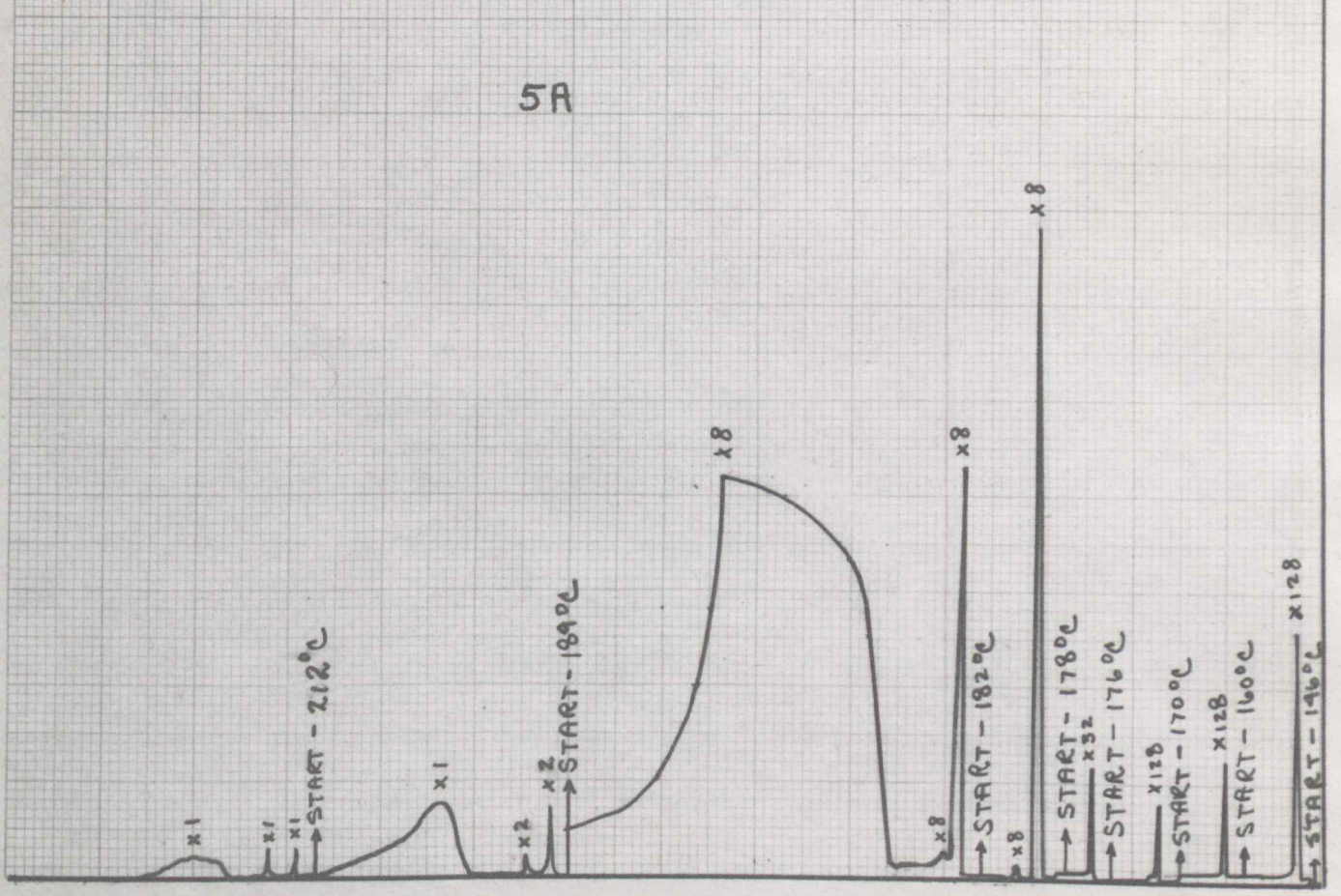
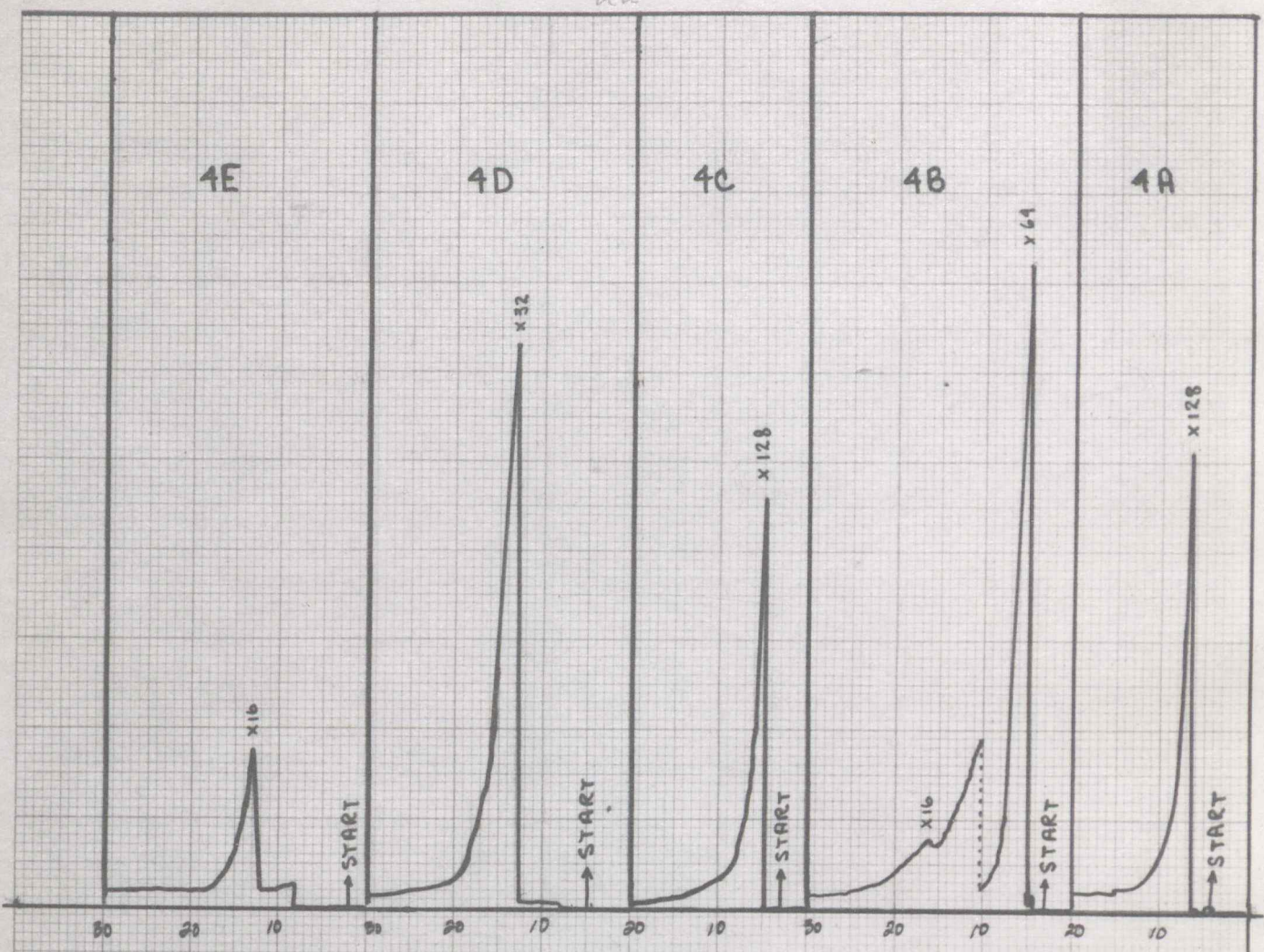
with two readily accessible oxidation states (11).

Another interesting aspect to study would be the effect of anti oxidants such as phenols and aromatic amines.

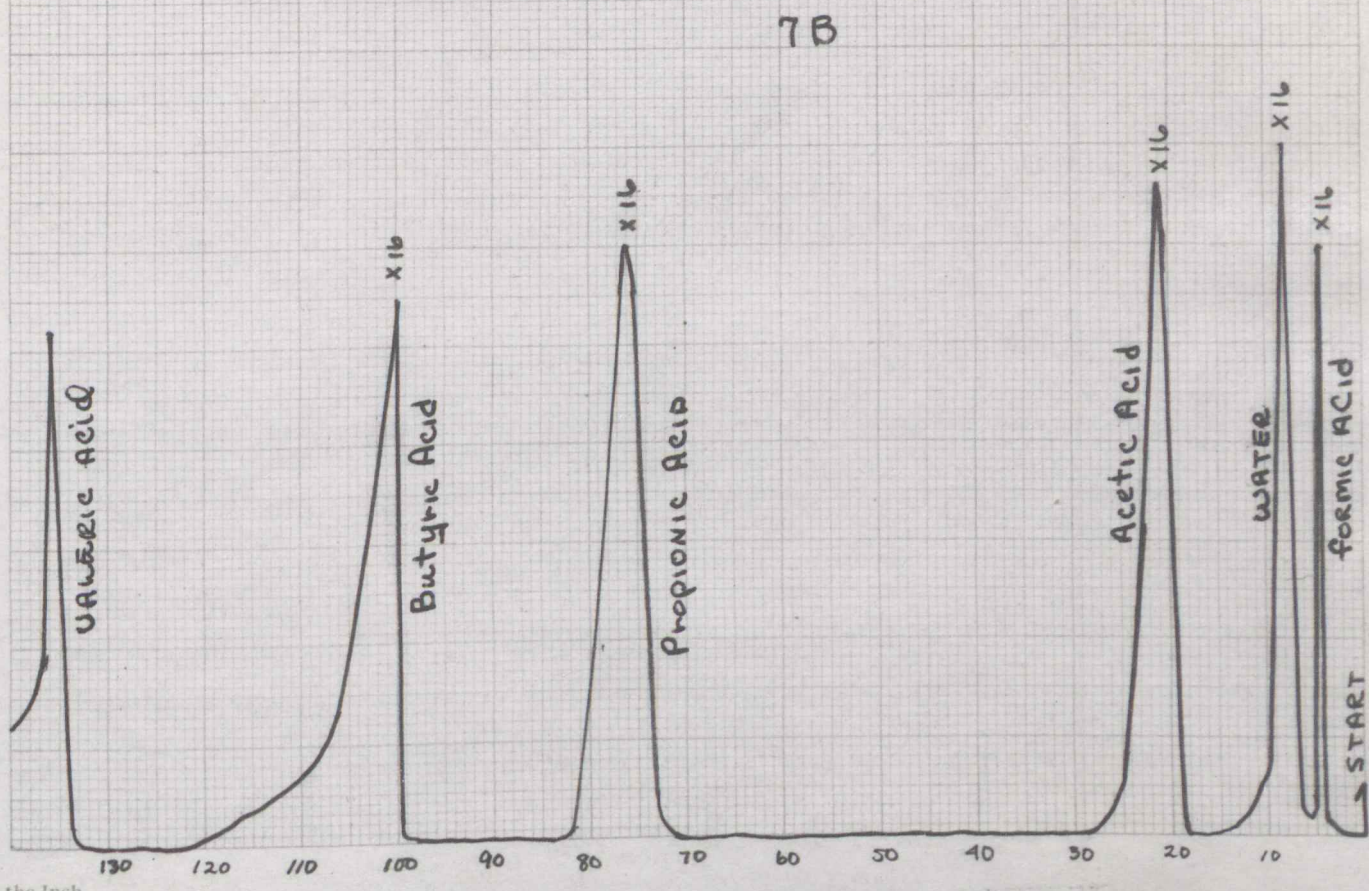
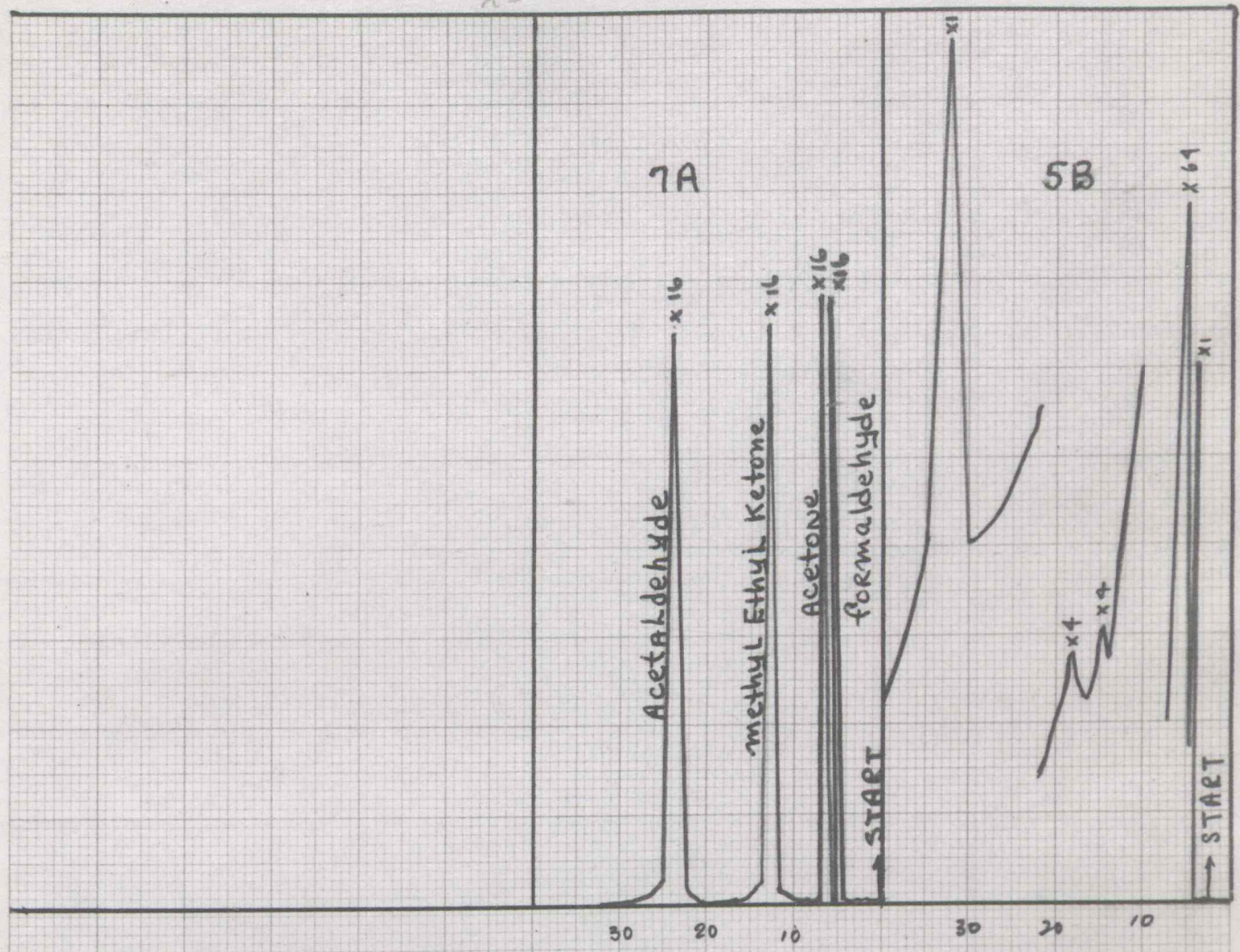








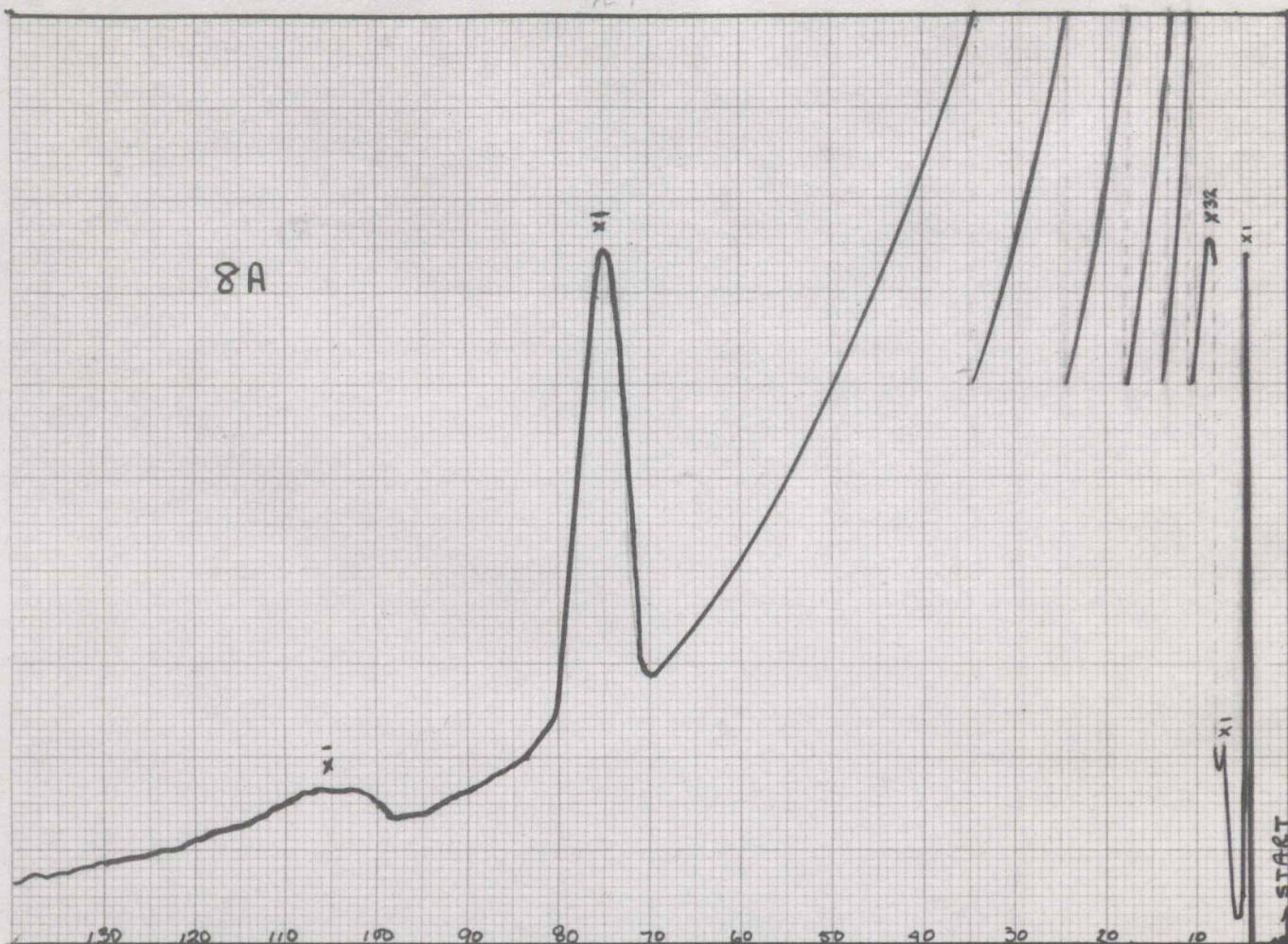




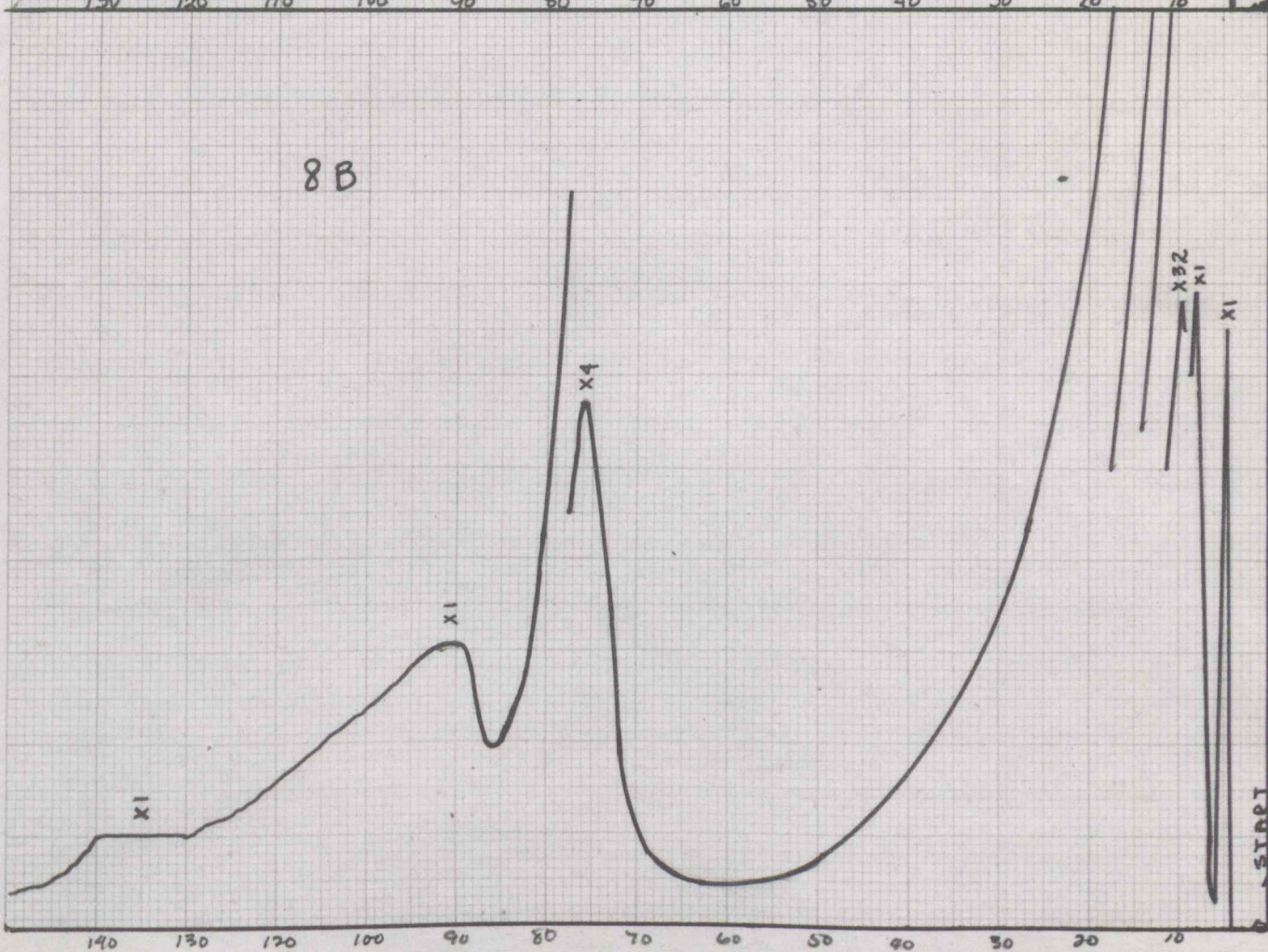


2A

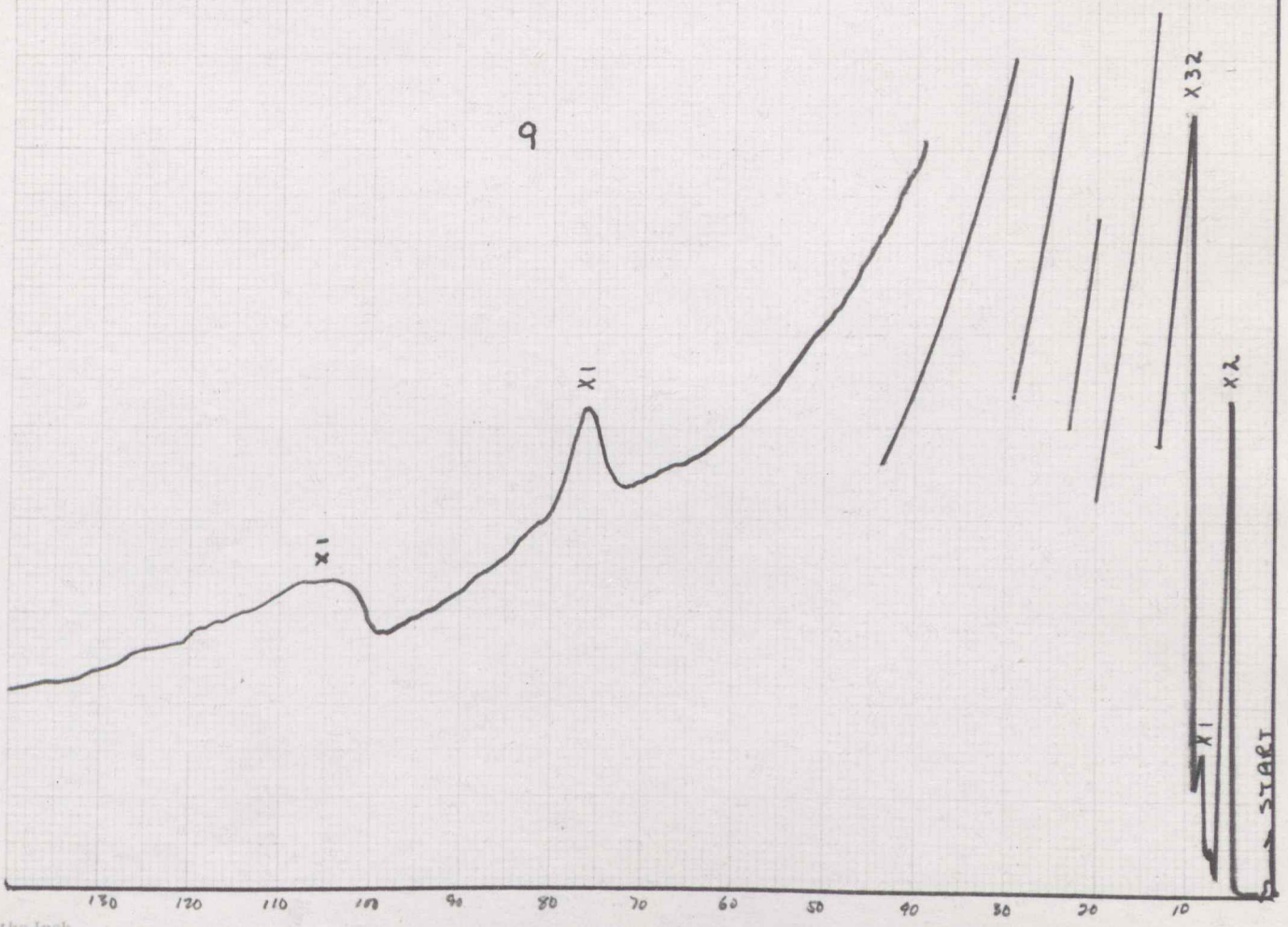
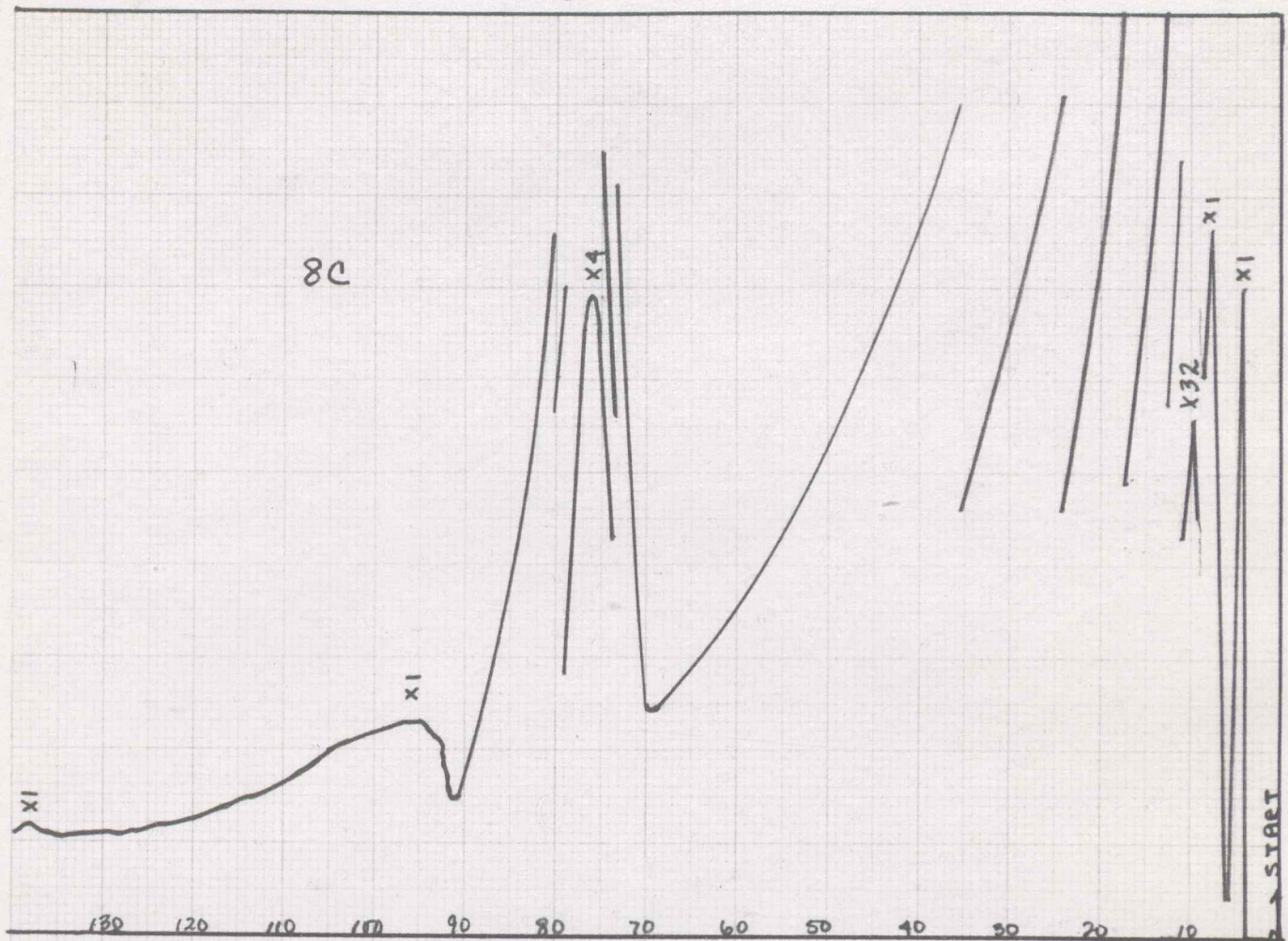
8A



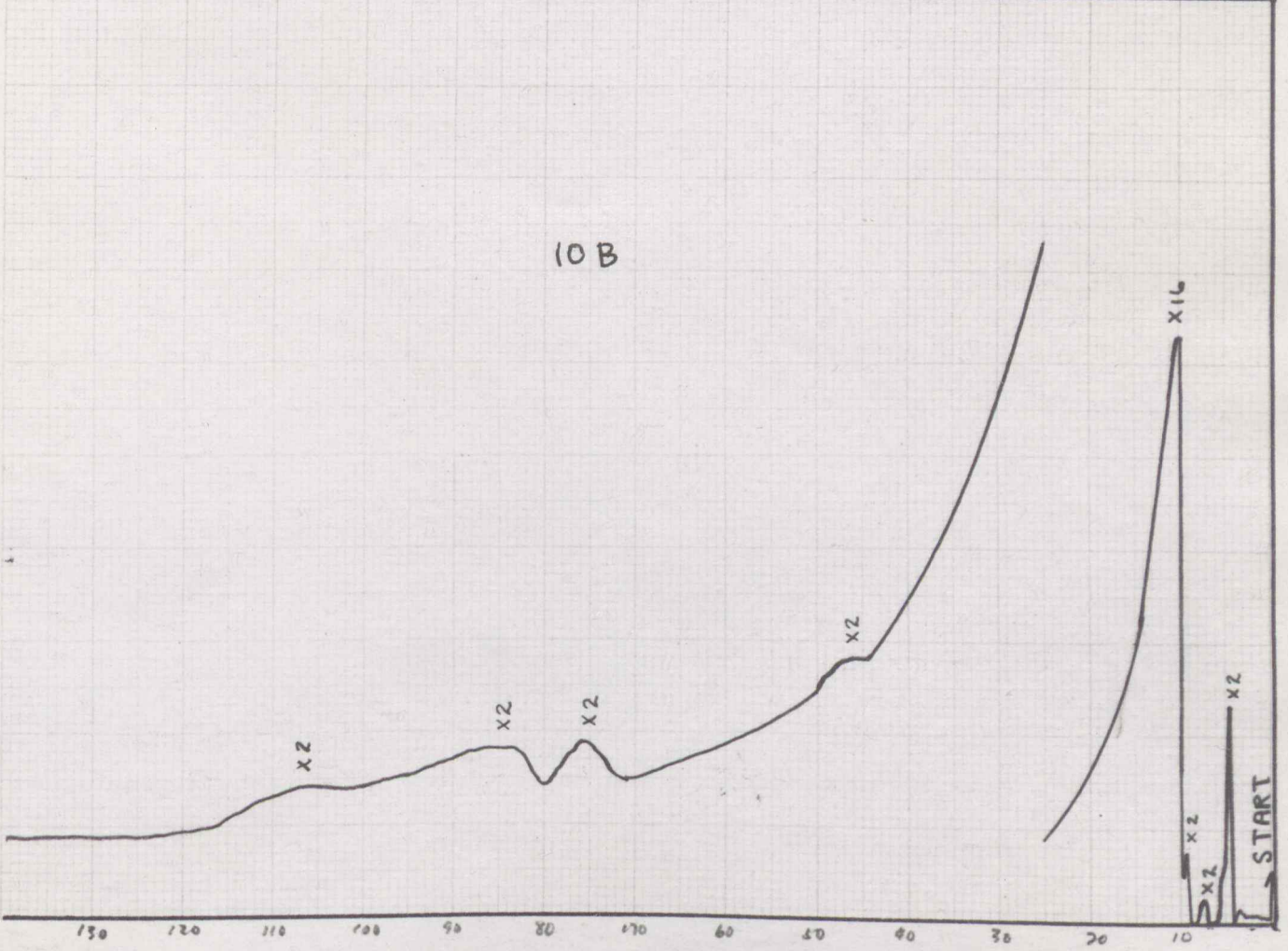
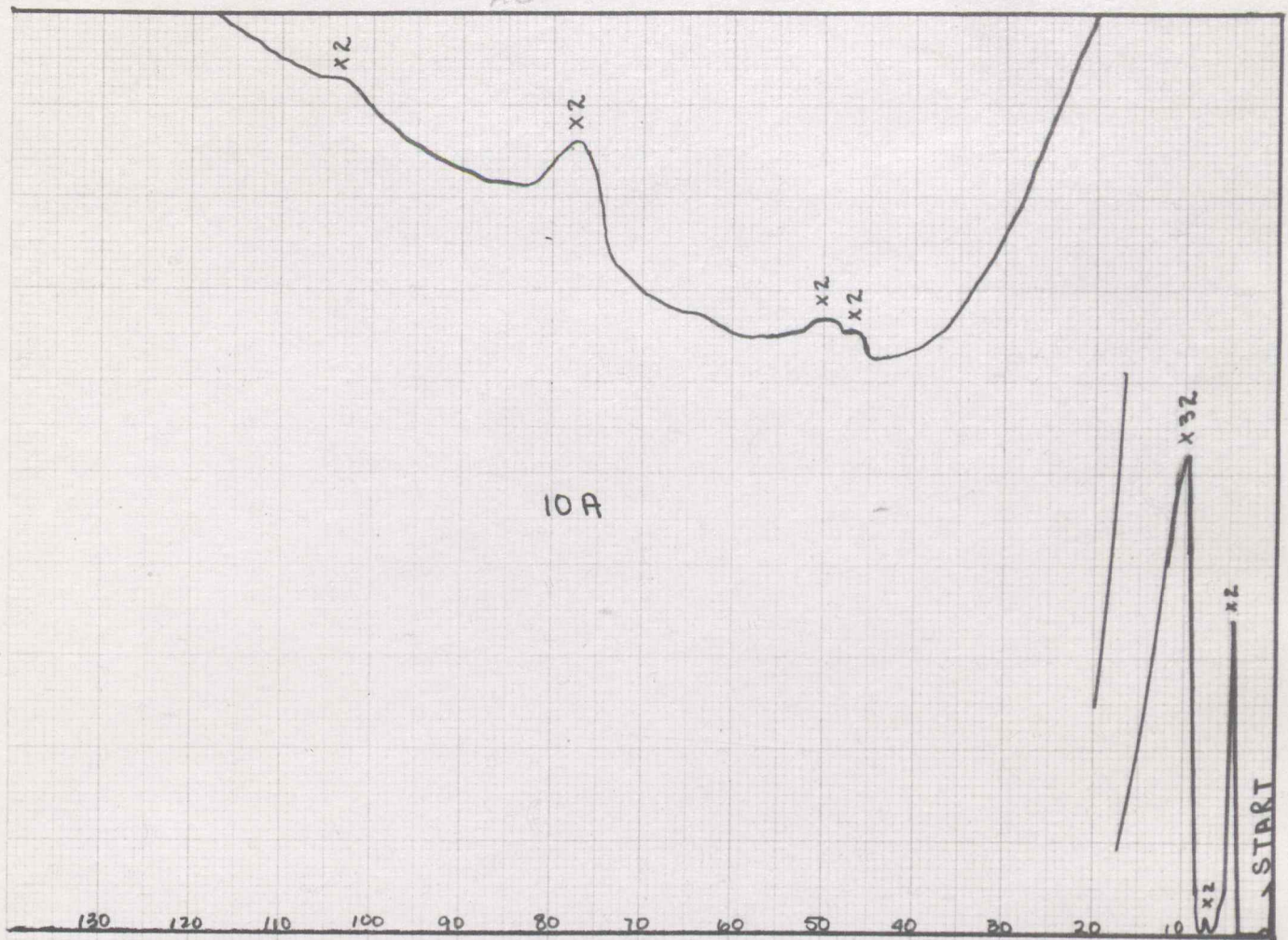
8B





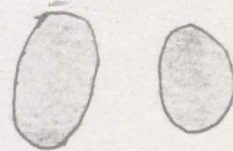
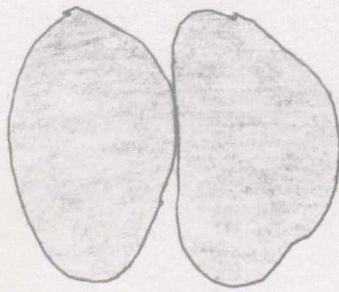






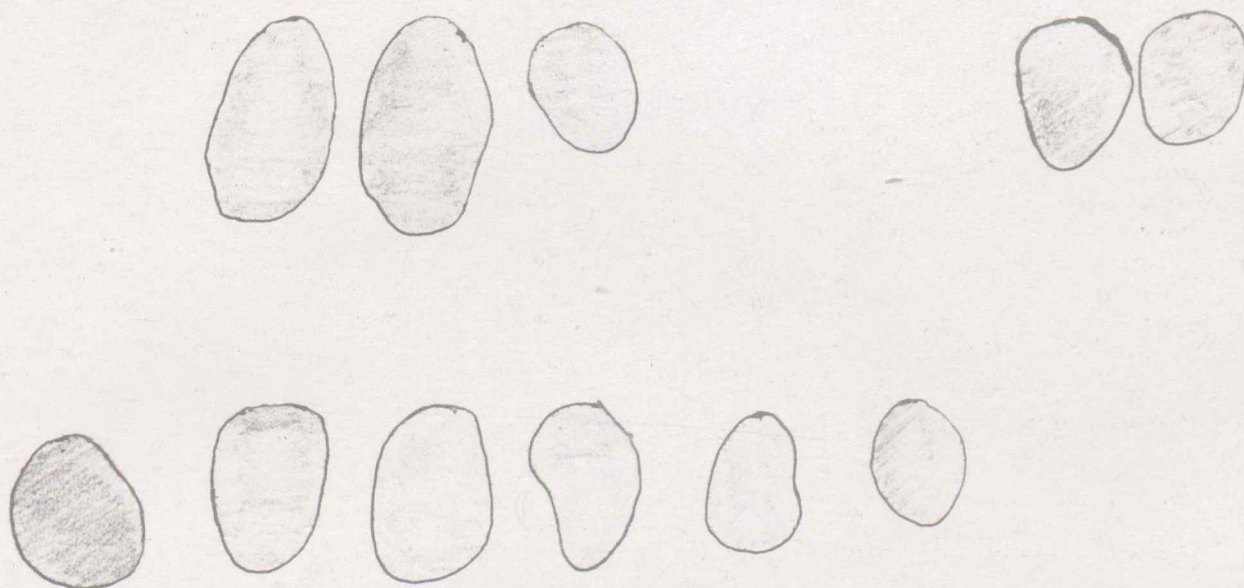


6A

acetic  
acidpropionic  
acidbutyric  
acidvaleric  
acidunkn  
#1unkn  
#2unkn  
#3unkn  
#4  
glucose

fructose

6B



unkn  
#4  
glucose

unkn  
#1

unkn  
#2  
fructose

unkn  
#3

formaldehyde

acetaldehyde

acetone

methyl ethyl  
ketone



Diagram 1

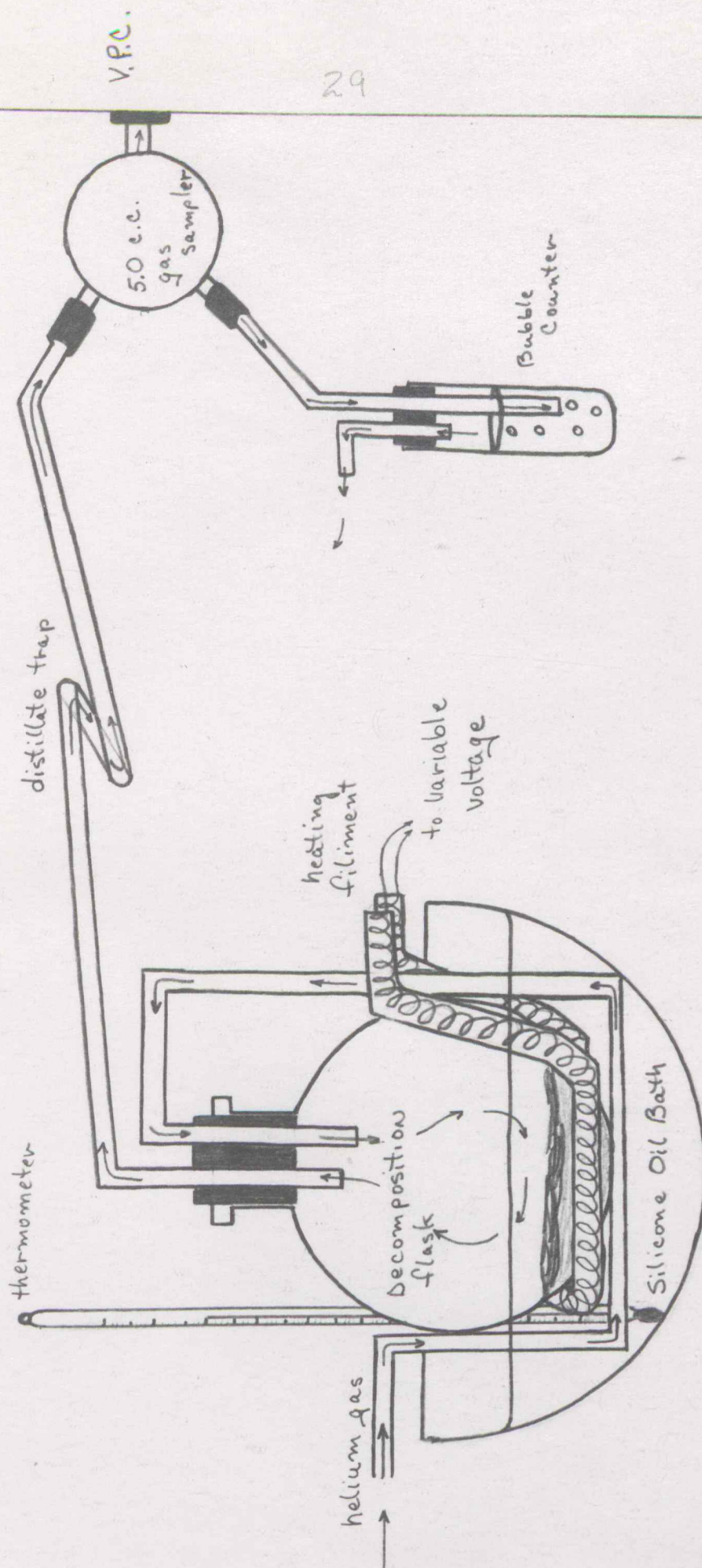


Diagram 2

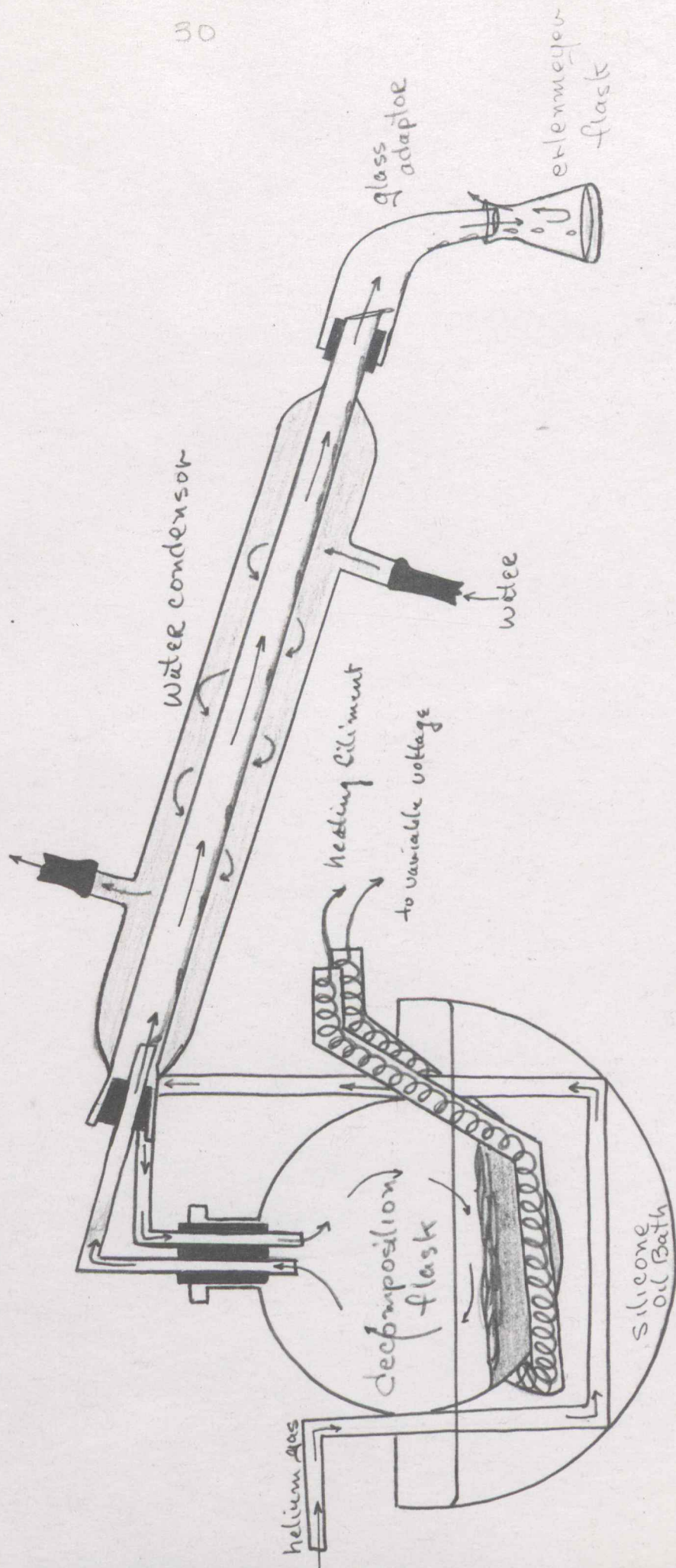
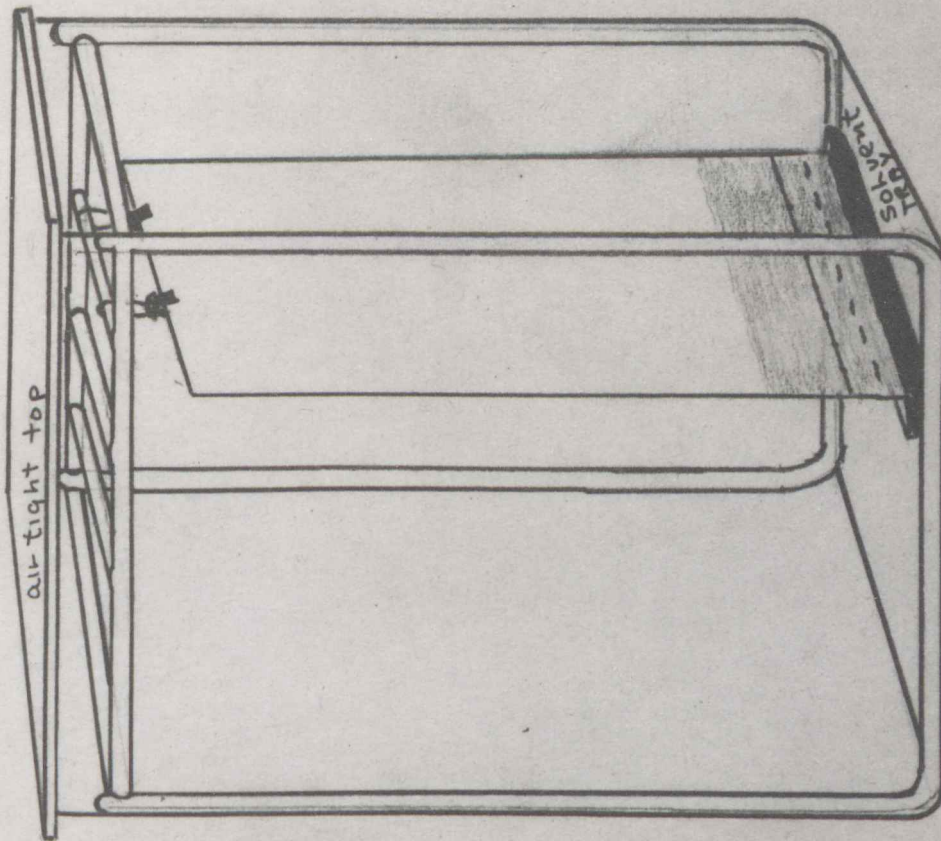
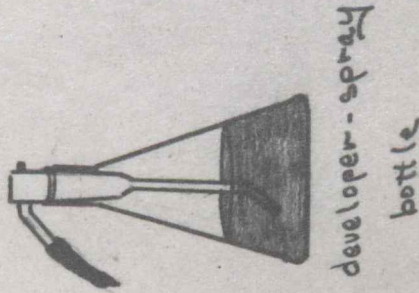




Diagram 3



tank designed for two demension,  
24 hr. paper chromatography



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