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A METHOD FOR
ATMOSPHERIC HYDROCARBON DETERMINATION

by

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A gas chromatographic method of analyzing trace constituents of volatile organics in the atmosphere has been developed, utilizing techniques of low temperature collection and sample concentration. Samples are collected using adsorption on an inert substrate at -77°C , while sample concentration is accomplished with liquid nitrogen as the coolant.

Samples have been taken from urban Boston out to forty-five miles north of the city. Over forty-five components have been seen in the samples. Composition of the city samples is similar, with fluctuations in quantity. Samples from the rural area appear to be of considerably different composition with a few similarities.

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Sometimes a person is like an old car -- it takes a big push to get started and encouragement to get over the hills. My thanks, Wayne, Jane, Phyllis, and Dr. Carritt.

TABLE OF CONTENTS

Abstract	i
Introduction	1
Background of Method	4
Experimental10
Procedure.12
Discussion13
Discussion of Results.16
Bibliography18

Urban life produces many strange effects on the population, both social and physiological. In the atmosphere most hydrocarbons are present on the .1 ppb to 1 ppm range. It is clear that biological activity and functions are regulated by trace amounts of certain substances. The pollutants being produced by man are no doubt producing chronic health hazards. Pollution is considered a nuisance but an unescapable adjunct to the way of life. The human body is a complex engineering marvel easily poisoned by foreign substances, and it is reasonable to assume pollutants will have adverse health effects. Strong steps must be taken for self preservation.

There are two main categories of the health effects caused by air pollution--acute and chronic. High concentrations of certain atmospheric pollutants produce acute sequelae in a significant percentage of the exposed population. These acute effects range from mere irritations of the mucous membranes of eyes, nose and throat to extreme respiratory distresses, sometimes even resulting in death. Hydrocarbons in high concentrations have a variety of harmful effects upon the body. In industries dealing with hydrocarbons and organic solvents the symptoms are clearly evident.¹ Hydrocarbons prove to be an acute narcotic producing severe and sometimes fatal depression of the central nervous system in quantities of from 600 ppm to several thousand ppm (E. Browning, 1953). Although there is not much data on ppb concentrations of pollutants, less prolonged exposures are said to produce various manifestations

¹Symptoms listed are from E. Browning, 1953, Toxicity of Industrial Organic Solvents.

of nervous and digestive disorders. Lungs showed the most severe and constant changes with emphysema and bronchitis common. The kidneys showed injury only with higher hydrocarbon concentration. Symptoms related to disorder of the central nervous system are headaches, giddiness, lack of sleep and anemia.

In the literature there is little agreement on the long term or chronic health effects of air pollutants in low concentrations. Understanding of the long term consequences to health of low level or everyday contaminations is a topic of much debate. The two respiratory diseases commonly mentioned in connection with air pollution, chronic obstructive bronchopulmonary disease¹ and pulmonary cancer, have no recognizable single cause. Multiple causes of these diseases and presence of multiple factors, capable of having causal significance, in the groups studied makes correlations extremely difficult and at best uncertain.

Slow changes in public health from air pollution must be occurring in a large number of people. The best place to start looking for symptoms would be the respiratory passages and lungs. Bronchitis and emphysema, commonplace disorders of the bronchial tubes and lungs, appear to be chronic effects of pollution, as is indicated by their increased number of occurrences (McDermott, 1961). Fortunately, man's stupidity has been compensated for somehow by meteorological conditions. Pollutants are dissipated by diffusion into the atmosphere and do not therefore reach lethal limits. On occasions where temperature inversions or other unfavorable conditions for dispersion of contaminants

¹Chronic obstructive bronchopulmonary disease is a term given to either chronic bronchitis or clinical emphysema, or both co-existing, in a patient.

exist for several days harmful effects are recorded. Two cases that reflect the severity of the pollution problem occurred in Donora, Pennsylvania in 1948 and in London in 1952. After several days of continued "smog" in Donora, 5,410 persons were reported ill and twenty persons died. In London there was an increase in the death rate of 4-5 thousand people in one week during which "smog" conditions prevailed. A continued study of Donora showed increased incidence of illness and mortality rate nine years after the incident (McDermott, 1961). If severe pollution can have such a drastic effect after several days exposure, what are the possible long range consequences at pollution levels only somewhat lower?

Hydrocarbon content is of particular interest because of its role in eye irritation and plant damage. Certain hydrocarbon components of automobile exhaust become involved in photochemical reactions when released into the atmosphere. Nitrogen dioxide absorbs UV in the regions of the spectra available near ground level at wavelengths shorter than 370 mu. Nitrogen dioxide readily dissociates into nitric oxide and atomic oxygen which in turn attack the hydrocarbons (Stephens), (Tuesday), (Leighton). The result is the formation of ozone and various oxidation and nitration products. It is the oxidation-nitration products and ozone which cause the irritations and damages.

Health reasons alone demand a further study of pollution and its effects. Hydrocarbon distribution in the atmosphere may serve as a tag to study air-sea exchanges and general circulation patterns. Man may gather a better understanding of his environment and what he is doing to it.

Chromatography, coupled with the selective subtraction methods for certain class compounds, dual column analysis and comparison of sensitivities of different detectors, has proved to be a sensitive and versatile method for separating and identifying many atmospheric contaminants.

Farrington, et. al. (1963), Bellar, et. al. (1963, 1962), Altshuller (1962) and Altshuller and Bellar (1963) have extended the limits of chromatographic analysis for detection and determination to better than a part per billion. Farrington, et. al. (1963) using concentration methods has identified components present in the atmosphere in a few parts per ten billion. Altshuller and Bellar (1963) point out that results for total hydrocarbons or organics determined with flame ionization or infrared analyzers may give erroneous results because of widely varying detector response for different species.

Limits of detection are a direct function of sharpness of separation, of various components in any mixture, which is highly dependent upon the proper selection of column packings. Choice of column packings for atmospheric work is a function of the components being studied. Tritolyl phosphate packed on chromosorb proves to be a good all purpose column (Williams, 1965) (Araki and Kato, 1962). Altshuller and Bellar (1963) used three different column types in their investigation. Molecular sieve 13X proved to give good separations for methane analysis. Ethane retention time on this column is several times greater than for methane. Methane, ethane and propane are not separated with the tritolyl phosphate column and appear as one component. The separation method of Altshuller and Bellar provides a specific and sensitive methane analysis. Silica gel columns

were used for the two-through five-carbon hydrocarbons while carbowax 1540 packed on firebrick was used to analyze for aromatic hydrocarbons.

Methane concentrations of Altshuller and Bellar (1963) varied from 3.69-1.15 ppm. Sample size was small (3.12 ml) and no concentration step was employed. Total sample of methane analyzed varies from 3×10^{-9} to 11×10^{-9} liters. (A quantity of this size is well within the limits of detection in our laboratory. Samples 4×10^{-9} l have been easily detected.) Concentrations of atmospheric methane are shown by Altshuller and Bellar (1963) to be, in Los Angeles and elsewhere, from five to ten times the estimated concentration of the methane derived from automobile exhaust emission. It is well known that methane is a natural constituent of the atmosphere and it is suggested that since the lowest methane concentrations reported are slightly greater than one ppm that the natural concentration may approach this limit. Concentrations of toluene and eight carbon aromatics reached 0.14 ppm. Higher carbon aromatics were not studied.

Williams (1965) has separated and identified a total of thirty-three different organic compounds in the atmosphere, using two column packings not exhibiting much selectivity, tritoly phosphate and didecylphthalate. Concentrations of compounds found are estimated to be within the 0.1 to 10 ppb range. Concentrations in different samples varied by a factor of twenty or greater, but the sample composition varied only slightly over the length of the study. No direct quantitative measurements were made.

Identification of the chromatographic components presents a formidable task. Absolute identifications can be made by means of infrared spectrometry or by mass

spectrometry. Availability of the necessary apparatus or practicality of application in conjunction with gas chromatography are limiting parameters. In the absence of infrared or mass spectrometry, several chromatographic techniques must be relied upon. Identification by these methods are not absolute. Several compounds may give the same responses to the given identification parameters and solution for the component would not be unique. The more techniques or different number of parameters, the more positive the identification.

Brown (1960), West, et. al. (1961), Raupp (1958) and Merritt and Walsh (1962) have shown that comparison of relative retention times for an unknown on different column packings can greatly aid in identification. By using standards and comparisons of retention on columns having varying selectivity for different class compounds, a reasonable identification can be made. As the number of columns increase, the identification becomes more valid. Any method aiding in the classification of the mixture is of importance.

Detector response proves to be invaluable in the aid to identification. The degree of specificity or sensitivity for class compounds between detectors is great (Lovelock, 1961). Klauss (1961) has reported the uses of this technique. Flame ionization detectors respond to all organic compounds except formic acid (Lovelock, 1961). Greatest response is given with hydrocarbons and decreasing response occurs with increasing substitution of other elements. This method is unsuitable for detection of halogenated compounds which exhibit electron capture and a great decrease in detector response. A special method

for the determination of these compounds has been developed owing to their ability to capture electrons--the electron capture detector. Hydrocarbons are not readily detected with electron capture because of the negligible affinity of hydrogen and carbon for free electrons. Organic compounds containing oxygen and halogens will capture electrons owing to the ease with which oxygen and halogens react with free electrons to form stable negative ions. Flame detectors employed with selective column analysis methods provide a powerful tool for compound identification for atmospheric hydrocarbon studies.

Extensive knowledge of the classes of compounds present in the chromatogram is gained through the use of subtractive techniques in which certain classes of compounds are selectively removed, either chemically or physically. Subtractive techniques can be applied at two points in the analysis. In the sample collection, selection of the drying agent is important. A division of compounds is accomplished by Williams (1965) using magnesium perchlorate and potassium carbonate as drying agents. Recovery over potassium carbonate is essentially complete for all classes of compounds (Farrington et. al. 1959) while magnesium perchlorate holds up such classes as carbonyls, ethers nitriles and nitro compounds. (Farrington, et. al., 1959) (Winters 1965) Farrington, et. al. (1959) have also studied several other subtractive compounds as drying agents. Most of these are not applicable to atmospheric work for a variety of reasons.

Subtractive methods are also used in conjunction with the separatory column (Hoff and Fert 1963, 1964) (Winters, 1965) (Brenner, et. al., 1960). Molecular sieves are used as subtractors in gas chromatographic analysis because they exhibit irreversible absorption of certain compounds

Brenner, et. al. (1960) showed that 5 A molecular sieves irreversibly absorbed all hydrocarbons, including normal olefins, normal alcohols, aldehydes and acids, except methane. Adsorption occurs according to pore openings of the molecular sieve. The larger the pore openings, the more adsorptive the sieve is. Wide varieties of molecular sieve available make it possible to select a given type which retains individual compounds in the simple, while others pass on to be chromatographed. Winters (1965) has deactivated the surface of the 5A molecular sieve by treatment with hexamethyldisilane. Winters reports that at low concentrations some compounds not reported to be adsorbed (Brenner et. al. 1960) were. Deactivation altered the character of the sieve and allowed passage of the aromatics. Concentrated sulfuric acid mixed with Chromosorb G was shown to have subtractive properties for certain alkenes, ethers, ketones and alcohols.

Collection of the samples presents another major problem in atmospheric work. Sampling methods are dependent upon the concentrations being looked at. Altshuller and Bellar (1963) were looking at a concentration range of from 5 ppb to 4 ppm. No concentration method for the sample was used and the sample of 3.12 ml. was collected directly on the chromatograph in a glass sampling line. Bellar, et. al (1963) made use of a collecting column with packing material. The column was cooled in liquid nitrogen but none of the lighter fractions were collected. Concentrations of iso-butane in 6.0 ppb were the first components in his 200 cc sample. Silica gel at dry ice and acetone temperature was found to be a satisfactory adsorbant for the concentration of hydrocarbons by Altshuller (1962).

For collection of the lighter fractions, ethane and ethylene, liquid oxygen was used as the coolant. Methane was only detected in small traces if seen at all. Araki and Kato (1962) quantitatively removed C_2-C_6 hydrocarbons by passing a 100 ml sample through a condensation tube packed with crushed firebuck and cooled with liquid oxygen. Methane could not be condensed at this temperature on the packing. Sampling was accomplished by Winters (1965) using partially deactivated Chromosorb at dry ice temperature. After collection of the sample the collector is heated and the sample trapped in a concentration step with liquid nitrogen. Direct analysis is then made on the concentrated sample. Techniques developed by Winters are used in this paper.

Figures 1 and 2 are schematic diagrams of the apparatus used in this study. The valve system designed leads directly to the chromatograph. Five 316 stainless steel toggle valves are used, enabling flow to be directed either through the chromatograph or through the concentration loop. With valves 2 and 3 closed and valve 1 open, flow is through the chromatograph alone. When valve 1 is in the closed position and valves 2 and 3 open the flow is through the loop and the sample is injected into the machine. It is important for good resolution that the sample be injected into the chromatograph as a slug not over a time interval. With this valve system there is no stoppage of the carrier gas flow during the time required to throw the valves for sample introduction. Stoppage of the carrier gas flow causes base-line drift which interferes with the earlier peaks on the chromatogram. Valves 4 and 5 are in the open position during concentration of the sample and closed during introduction and running of the sample.

The collecting column (Figure 2) consists of a six inch length of 3/8 inch o.d. 304 stainless steel tubing silver soldered to a length of 1/8 inch o.d. 304 stainless steel tubing. Two Whitey brass toggle valves are connected to the tubing with Swagelok fittings. Better peak resolution is found with the straight tube than the conventional U shape (Winters, 1965). Packing of the column consists of Chromosorb P partially deactivated with 5 or 10 per cent dibutylphthalate depending upon which collector is used. To prevent irreversible adsorption of polar compounds deactivation is necessary (Winters, 1965). All six inches of the 3/8 o.d. tube were packed except for two plugs of glass wool. A Dewar flask filled with dry ice is used as the coolant during sample collection. Another Dewar, filled

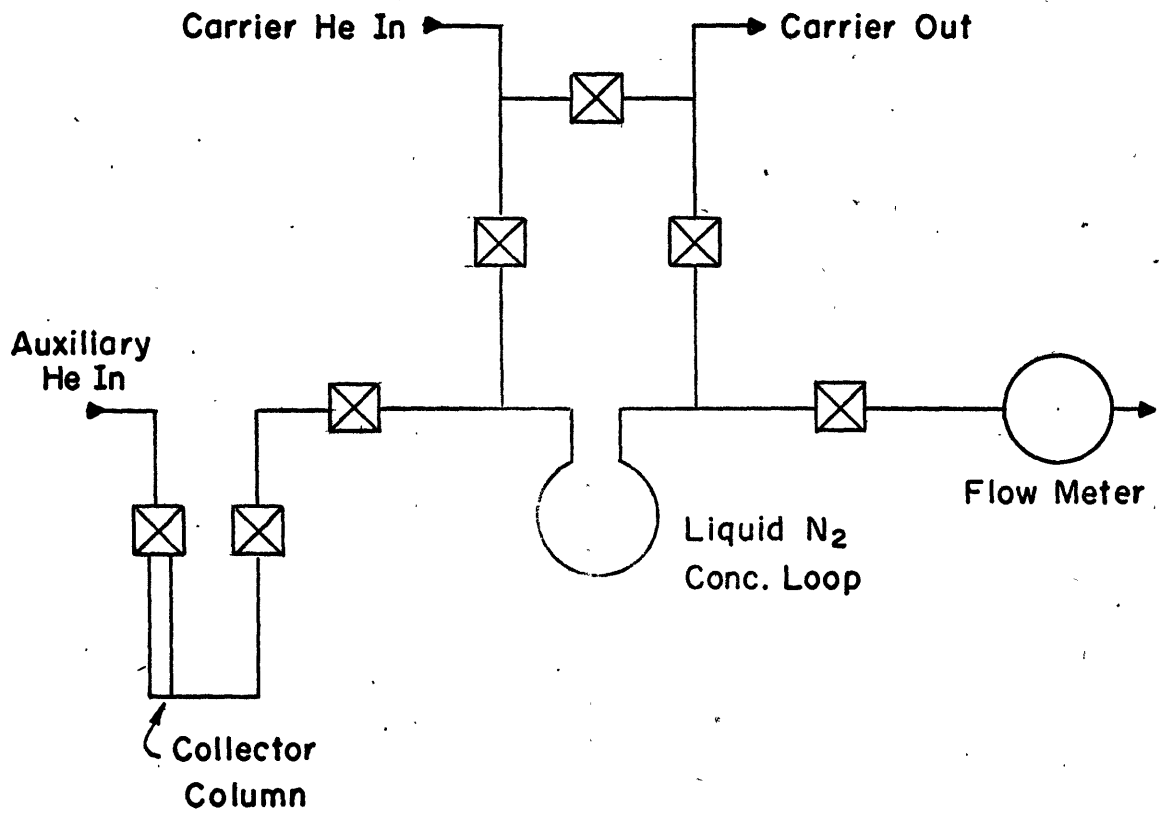
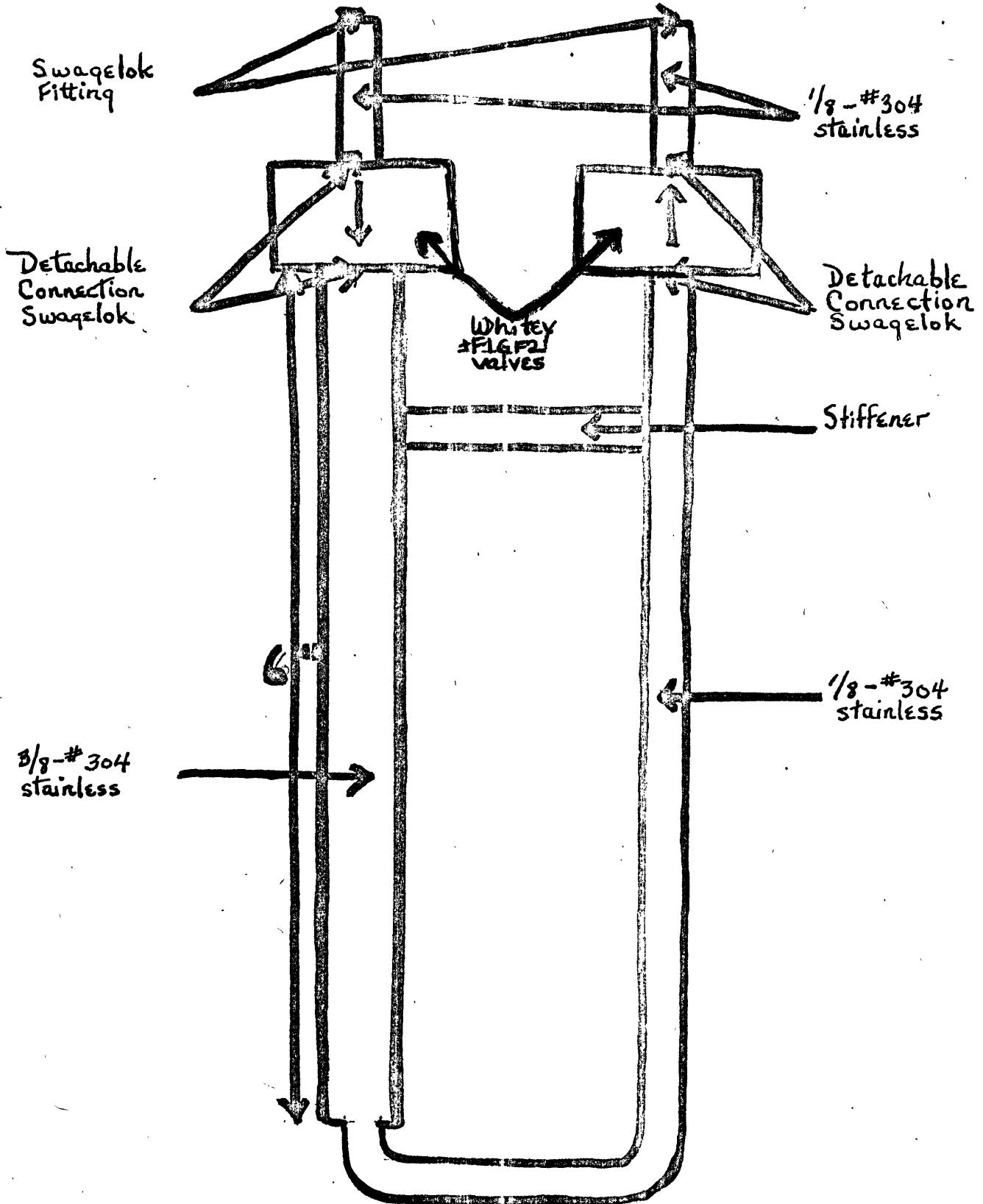


Fig. 1 VALVE SYSTEM FOR COLLECTOR

Figure 2 Gas Sample Collector



with liquid nitrogen, is used to cool the 10 ml stainless steel loop during concentration of the sample. The column is heated to 170°C with a heating tape wrapped around the collector and controlled with a Variac. Heating of the concentration loop is accomplished with a hot air blower operating at approximately 210°C. A heat shield of aluminum foil is used to cover the valve system to provide greater heating, eliminating the possibility of condensation of the sample. Insulation of fiberglass sheeting is placed between the hot air blower and the electrometer unit. It was observed that the indirect heating of the electrometer unit caused erratic shifts in the baseline which could not be stabilized. Better stabilization in baseline is obtained if the flame ionization detector is operated at high temperatures. Condensation and consequent contamination of the detector probably occurs at lower temperatures, providing large amounts of bleed off.

The two column packings used in this work were twenty per cent tritoyl phosphate by weight on 60/80 mesh acid-washed Chromosorb W and twenty-five percent didecylphthalate on 60/80 mesh acid washed Chromosorb P. Both columns were packed in 1/8 inch o.d. 316 stainless steel columns 10 feet in length. Operating temperature for the tritoyl phosphate column was 75°C. Packing was prepared using the technique described by Parcker and Urone (1964).

Samples are collected by drawing the air, with a portable vacuum pump, through the collecting column packed in dry ice. The column is allowed to come to thermal equilibrium with the ice, a period of about ten minutes, before the sample is taken. A drying column of potassium carbonate is placed before the vacuum pump. Sampling consists of 12.5 liters for the city samples and 240 liters for the rural sample. The sample is kept in dry ice until it is ready to be analyzed.

After collection the sample is connected to the valve system as in figure 1. While the sample is still packed in the dry ice purified helium is passed through it to displace any air trapped. Helium is purified by running it through a cold trap consisting of Chromosorb W packed in a ten foot long 1/4 inch column and cooled with liquid nitrogen. The sample collector is then heated for 15-30 minutes while the concentration loop is cooled with liquid nitrogen. The loop is then heated for 2-5 minutes and the sample introduced into the chromatograph by throwing the valves, diverting the carrier gas flow through the loop.

Before each sampling period the above procedure is carried out in each collector. The samplers are heated at 170°C while being flushed with helium until the resulting chromatograms have a stable base line.

The degree of specificity exhibited by the tri-tolyl phosphate columns for the lighter fractions of components is not very great--as evidenced by the separations in chromatograms 1, 2 and 3. Detailed studies of these components require better selection of column material. Comparison of relative retention times for the lighter components are not very meaningful because of the poor separations.

Identification of the components will be facilitated with the use of an electron capture detector in conjunction with the flame ionization detector. (Previously in this paper relative detector responses were discussed.) Compounds presently not detected in this study may be appreciable in the atmosphere. Flame ionization is not sensitive to halogen substituted compounds which would be expected to be present in a wide variety of compounds.

Chlorine and bromine, naturally present, and from automobile exhaust, react with hydrocarbons photochemically under the influence of short wave length (250-500 m μ) radiation or thermally at high temperatures. The photochemical reactions are not very selective and all types of hydrogens are attacked with equal ease. Introduction of one halogen atom does not affect the process of a second hydrogen atom replacement to a great degree. Almost all of the possible nonsubstituted products as well could be expected in a mixture.

Efficiency of the trapping system and elution of the sample are among the parameters to be considered in this study. Elution half time for the samples when elution flow was in the direction of sampling flow was fifteen minutes. This indicates that sample collection

is only taking place on a small upper portion of the packing material for most substances. If the lighter fractions are to be seen the additional column material is necessary. Presently it is doubtful if the total concentration of methane is collected at the cooling temperatures being used. If the amount of column packing were reduced methane, ethane propane and ethylene would not be detected. The elution with the collector in a reversed position, helium flow was from the bottom of the column instead of from the top, was essentially complete after a ten minute heating period. Again this supports the idea that the heavier portion of the sample, at least, is collected on the upper portion of the packing. The length of the collection column and the heating times required for complete elution of sample indicate that efficiency of the collection system is probably near 100 per cent for the heavier components. Collection of standards, using the method of sampling, supports this view. Since resolution of the chromatograms for the fractions below pentane is poor, efficiency checks are not precise. It is certain from the values obtained that efficiency is no greater than from 10-50 per cent.

Comparison of relative retention times for standards injected into the loop, and for identical peaks of the samples indicate that no sample holdup is taking place in the valve system. Relative retention values agree to better than two per cent. Relative retention times for peaks that cannot be positively said to have identical shapes but appear similar may differ by more than 4-5 per cent. This can either be caused by a possible sample holdup in the injection system or

Table Number 1

Run #3 -- Sample #3
 Taken Friday, 20000 Hours
 Massachusetts Institute of Technology
 Parking Lot
 Medium Rain

<u>Peak #</u>	<u>Position</u>	<u>Relative Position to Peak #30</u>	<u>Height</u>	<u>Comments</u>
1	.15	.00307	3	
2	1.47	.0301	130	Shoulder
3	1.8	.0369	170	
4	2.67	.0447	54	
5	3.15	.0645	94	
6	3.5	.0717	66	Shoulder on 5
7	4.20	.0861	46	
8	4.25	.0871	86	
9	4.61	.0954	94	
10	5.40	.111	102	
11	6.23	.128	84	
12	6.8	.139	---	Shoulder
13	7.4	.152	40	
14	7.88	.161	36	
15	8.62	.177	50	
16	9.74	.200	14	
17	11.22	.230	124	
18	11.9	.244	---	Possible Peak on Shoulder
19	12.95	.265	80	
20	14.7	.301	34	
21	17.0	.348		Trace
22	17.9	.367		Trace
23	19.4	.398		Trace
24	23.5	.482	44	
25	26.5	.542	93	
26	32.76	.671	5	
27	27.36	.765	8	
28	41.16	.843		Shoulder
29	44.86	.919	9	
30	48.76	1	19	Reference
31	57.36	1.17	5	
32	61.36	1.26	9	
33	65.96	1.35	12	
34	77.26	1.58	8	
35	81.86	1.68		Shoulder
36	91.16	1.87	11	
37	101.06	2.07	6	
38	108.26	2.22	5	
39	119.26	2.44	11	
40	126.66	2.64		Negligible
41	154.06	3.16	7	
42	171.76	3.52		Negligible
43	254.96	5.22	10.5	
44	300.86	6.15	3	

Table Number 2

Run #4 -- Sample #4
 Taken Monday Morning, 0300
 Massachusetts Institute of Technology
 Bottom of Building 54

<u>Peak #</u>	<u>Position</u>	<u>Relative Position to Peak #33</u>	<u>Height</u>	<u>Comments</u>
1	1.24	.02145	.6	Shoulder
2	1.52	.0262	9	
3	1.80	.03114	18	Shoulder
4	2.06	.03564	27	
5	2.24	.03875	20	Shoulder
6	2.66	.04607	18	Shoulder
7	2.92	.05052	35	
8	3.18	.0550	27	
9	3.46	.0599	30	
10	3.86	.0667	24	
11	4.22	.0731	22	
12	4.68	.0810	42	Double Peaks
13	4.72	.0817	43	Double Peaks
14	5.80	.100	51	
15	5.98	.103	126	
16	6.44	.111	62	Shoulder
17	7.60	.131	42	Shoulder (on a shoulder)
18	8.38	.145	29	
19	8.90	.154	26	
20	9.84	.170	16	With straight Shoulder
21	11.18	.193	13	Shoulder
22	12.66	.219	25	
23	14.48	.251	9.5	Edge of Shoulder
24	20.80	.360	.5	Trace
25	21.88	.379	2.5	
26	26.88	.465	24	
27	32.28	.558	9	
28	36.80	.637	2.5	
29	46.28	.801	6.5	Shoulder
30	49.28	.853	3	
31	52.68	.911	4.5	
32	55.80	.965	5	
33	57.80	1.00	10	Reference
34	67.88	1.17		Negligible
35	71.80	1.24	3	
36	77.88	1.35		Negligible
37	91.28	1.58	2.5	
38	103.28	1.79	3	
39	116.28	2.01	.5	Negligible
40	124.88	2.16	1	
41	138.48	2.40	2.5	
42	181.80	3.15		Negligible
43	184.88	3.20	1	

Table Number 3

Run #5 -- Sample #5
 240 liters Sample from Rural Atmosphere
 Approximately 45 Miles From City
 (Matson)

<u>Peak #</u>	<u>Position</u>	<u>Relative Position to Peak #29</u>	<u>Height</u>	<u>Comments</u>
1	.12	.00213		Trace
2	1.30	.0231	10	
3	1.64	.0291	14.5	
4	2.14	.0380	8	Shoulder
5	2.76	.0490	5.5	
6	3.24	.0570	6	
7	4.00	.0710	4.5	
8	4.60	.0817	7.5	
9	4.88	.0867	11	
10	4.98	.0885	17	
11	5.92	.105	13	
12	6.92	.123	34.5	
13	8.56	.152		Unattenuated
14	11.22	.199	31.5	
15	12.62	.224	13.5	
16	14.12	.251	20.5	
17	15.14	.269	30.5	
18	15.24	.271	9.5	Shoulder (Trace)
19	20.30	.361	1	Trace
20	21.30	.378	1.5	
21	23.56	.418		Negligible
22	26.50	.471	6	
23	30.76	.546		Unattenuated
24	40.70	.723		Negligible
25	44.30	.787	4	
26	48.10	.854		Negligible
27	51.50	.915	3	
28	54.10	.961	4	Shoulder
29	56.30	1.00	9	Reference
30	72.30	1.28	5.5	

result from different components. Since the comparisons of relative retention times for several components on the chromatograms are better than two per cent, it appears reasonable to assume that differences greater than five per cent indicate different fractions. Further investigation of the valve system must be made to eliminate any doubt that it may be responsible for a portion of the holdup.

Retention time for the operating conditions is extremely long for several components. This is undesirable as it limits the number of analyses able to be done. For the tritolyphosphate column the maximum operating temperature is only 125°C. The separations for the lighter fractions require low temperatures, however temperature programming for the heavier fractions will prove valuable in the small available temperature span.

Samples taken in the city consisted of 12.5 liters while the rural sample was 240 liters. Concentrations in city samples showed that the lighter fractions are from 80-180 times greater than in the rural sample. Heavier components in the two city samples are absent in the rural sample. Two areas in the rural atmosphere (peaks number 13 & 23 of Chromatogram 3) are equal in concentration to or greater than their counter parts in the city chromatograms (Peaks 25 and 13 chromatograph 1 and peaks 19 and 27 chromatograph 2). The city samples also appear to contain several lighter fractions not identified in the rural sample.

Presence of a greater number of the lighter fractions and their predominance in quantity in the city collections indicates that they can most probably be attributed to factors of urban living--automobile exhaust and industry. Concentrations in the city sample lighter fractions vary by a factor of 2-8. Sample 1 was taken on a Friday evening when there was considerable activity in the parking lot, while sample 2 was taken on a Monday morning at three a.m. when activity was at a minimum and pollution from automobile exhaust is expected to be negligible. Several peaks appear in chromatogram 2 not apparent on chromatogram 1. On Monday morning there were odors resembling burnt wood and chocolate present. Pollution from auto exhaust in sampling time 1 is not expected to be at a maximum. Many pollutants were probably washed out of the atmosphere by the relatively severe rain and traffic was definitely not heavy.

Complex nitration and oxidation products of automobile exhaust emissions probably represent the compounds with long retention times. Aromatics in polluted atmosphere constitute a significant part of the total hydrocarbon content. These compounds exhibit long retention times on the tritoyl phosphate columns and probably also represent the longer retained peaks on chromatographs 1 and 2.

The large concentrations of several components in the rural sample probably represent natural products--terpenes and terpene derivatives. The large fluctuation of the values of these peaks in the city samples cannot be accounted for if they are natural products, on the basis of the sampling conditions.

Pollution is not ruled out in the sample taken outside the city. The sampling location could have received wind drift, and it was only ten miles from a major road. A major problem is how to distinguish natural from man made pollutants. Studies of health effects of hydrocarbon pollution depends upon a quantitative positive identification of the components.

Quantities of organics seen in this study are estimated on the basis of standards, to be in the .01 ppb to several ppm range, which while not directly hazardous to health may produce irritation and long term discomfort and disorders.

Chromatogram #1

Detector 240°C

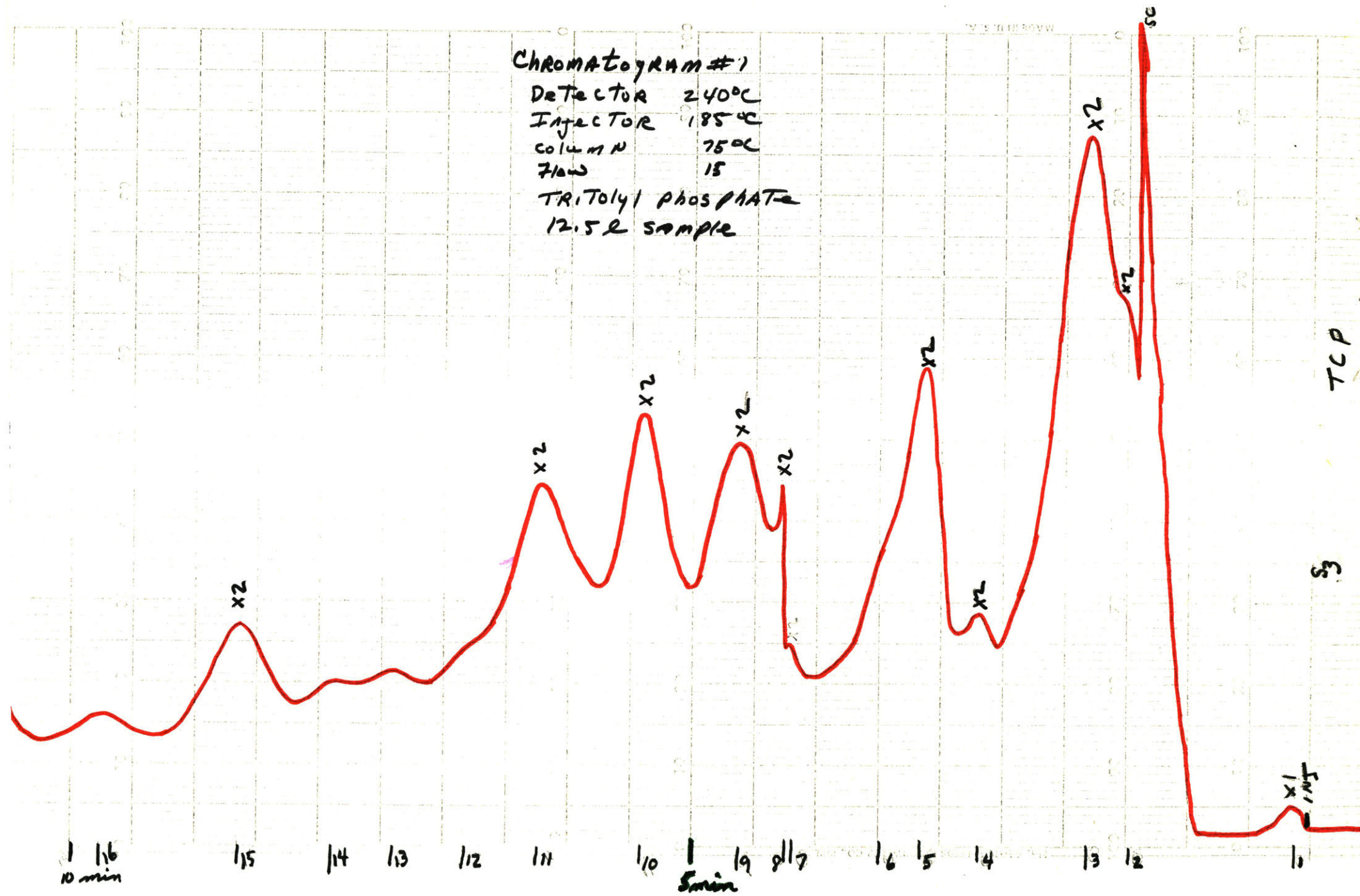
Injector 185°C

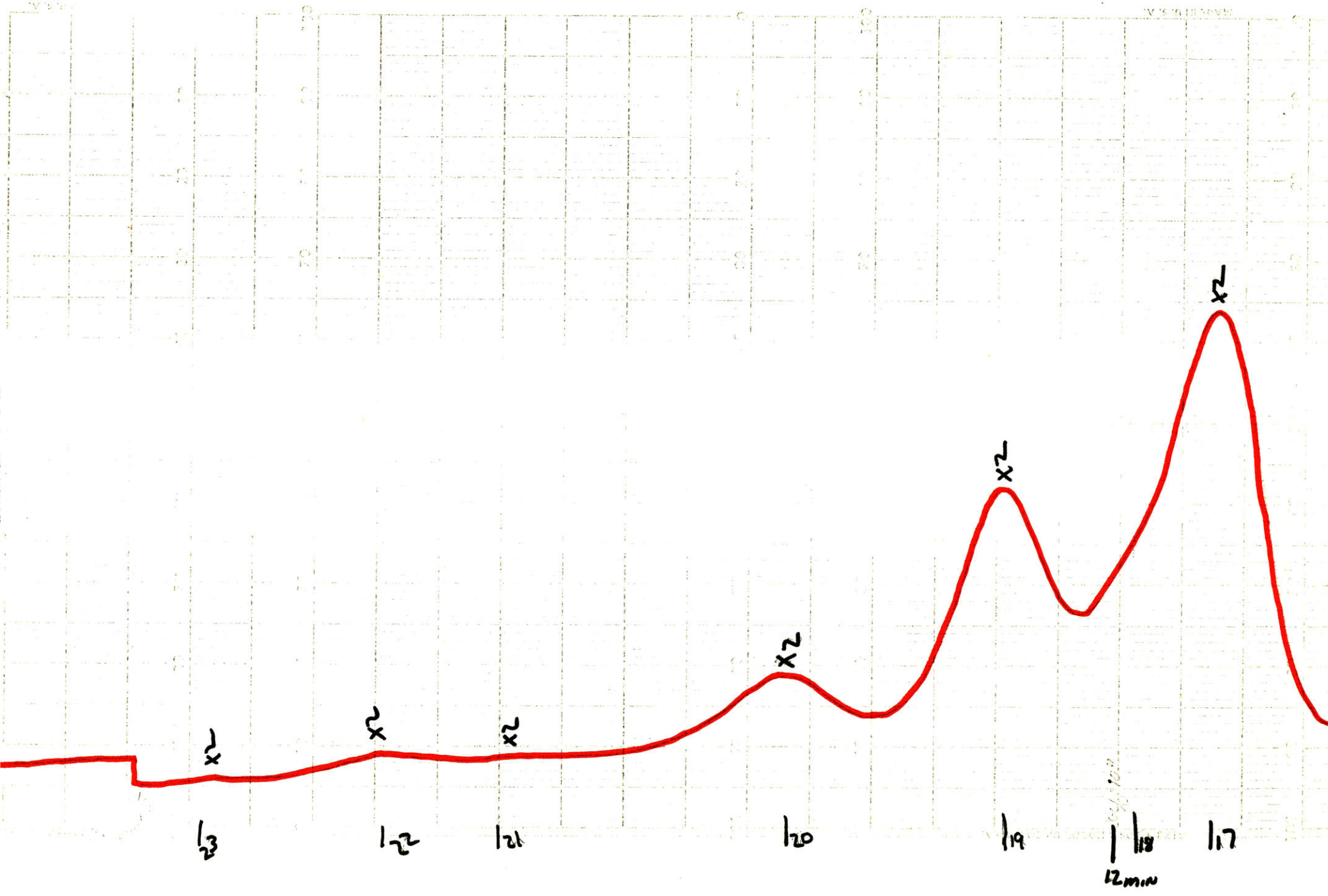
column N 750L

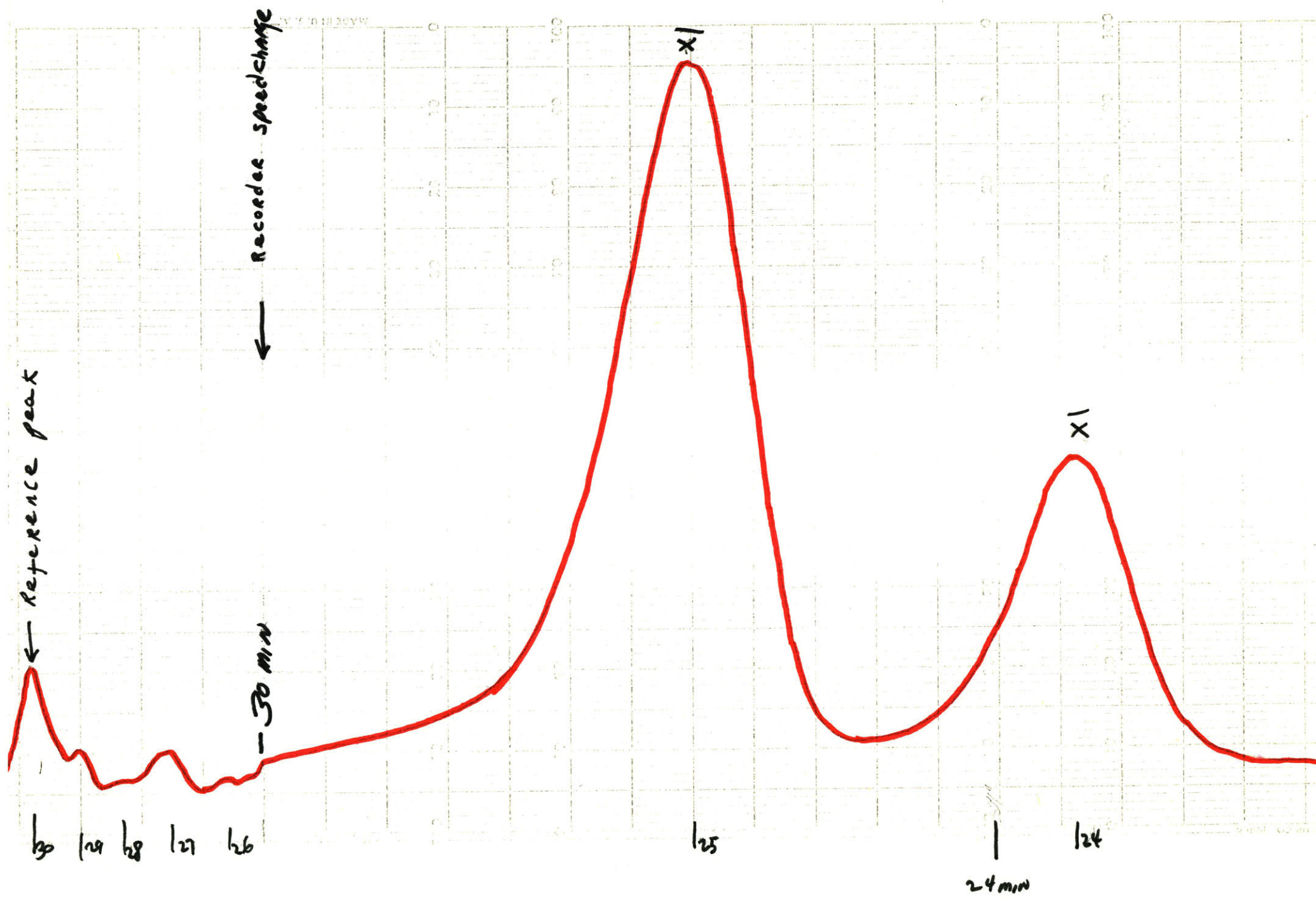
Flow 15

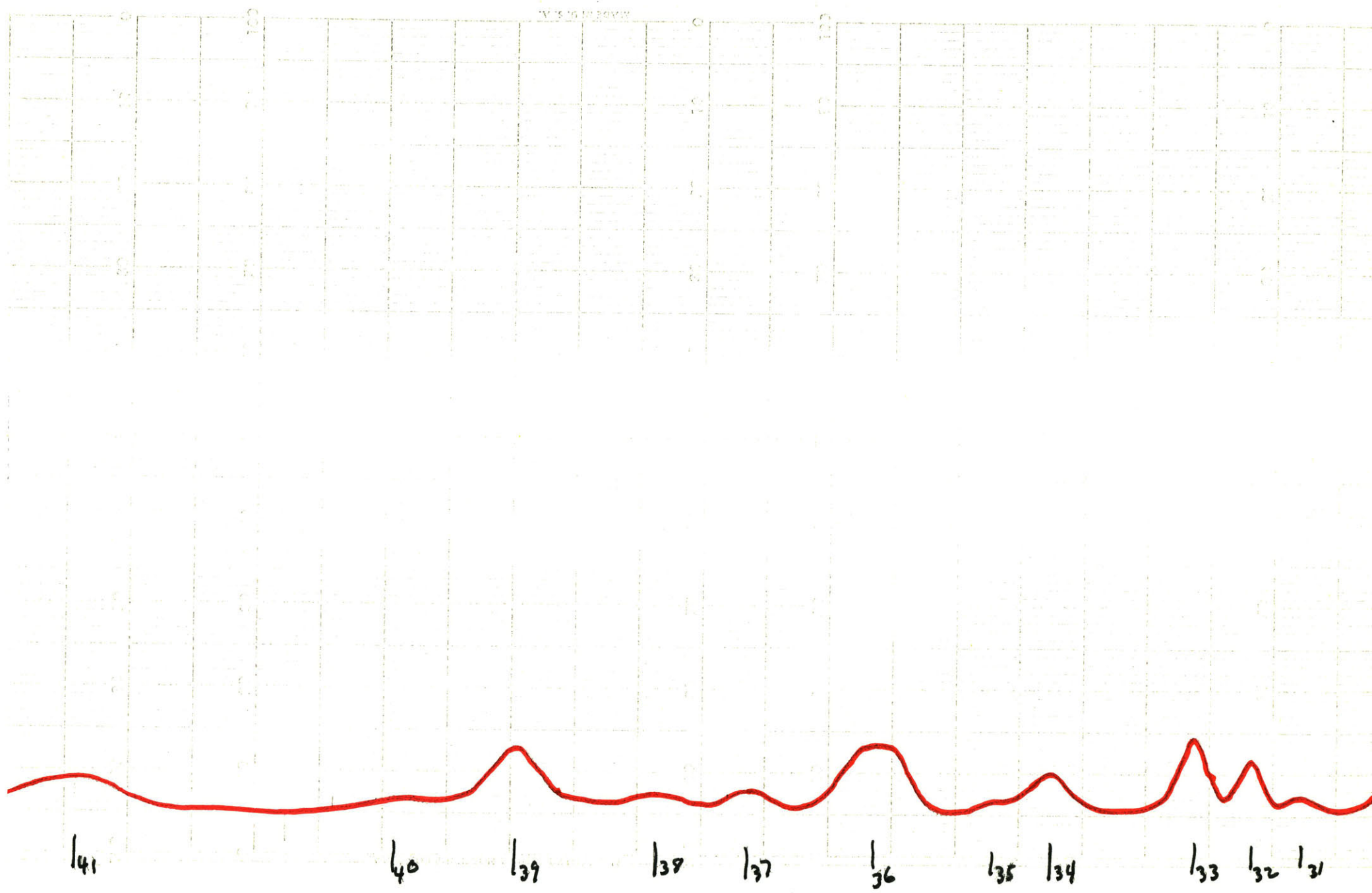
TRITOLYL PHOSPHATE

12.5 μ sample

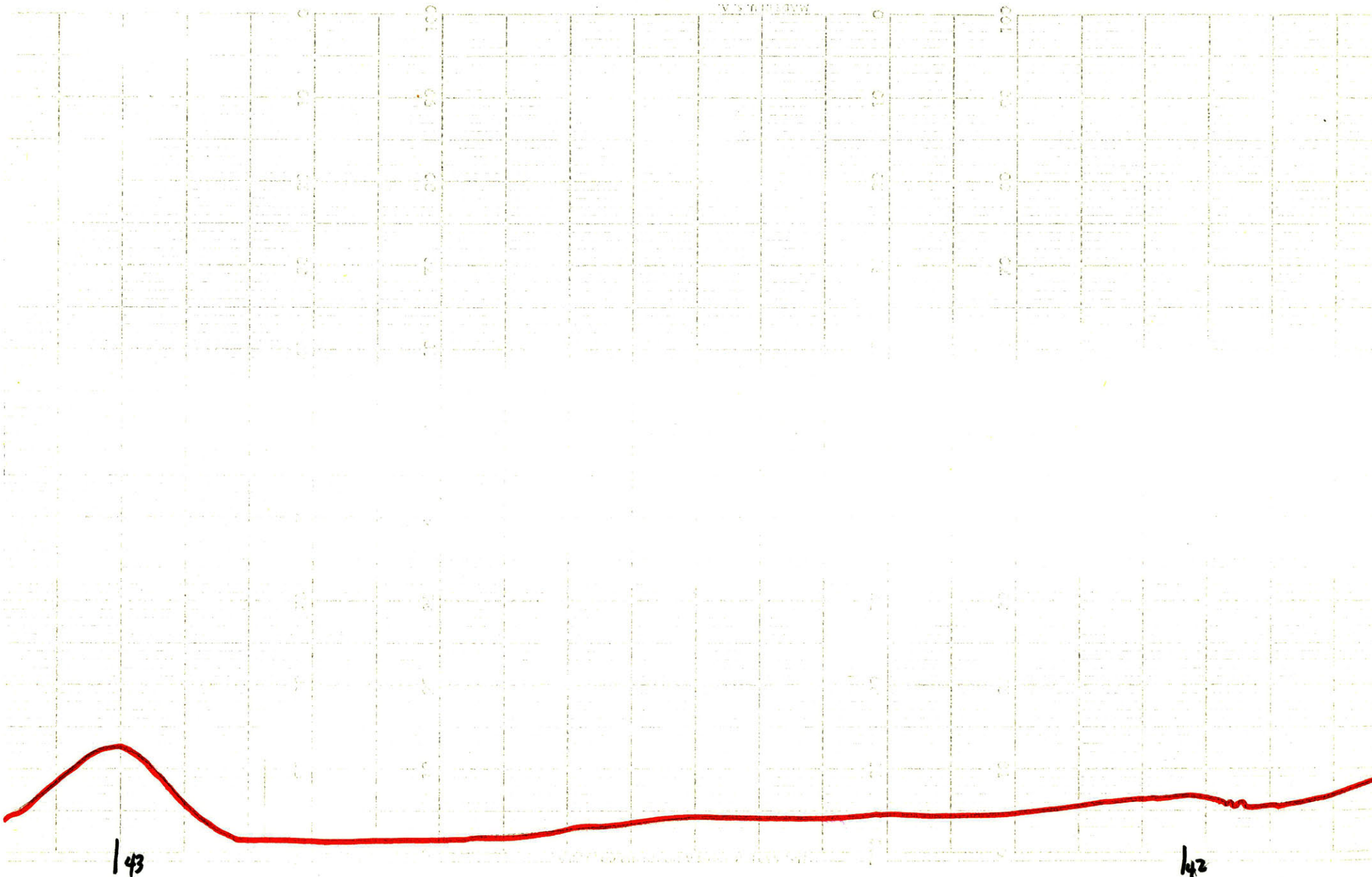








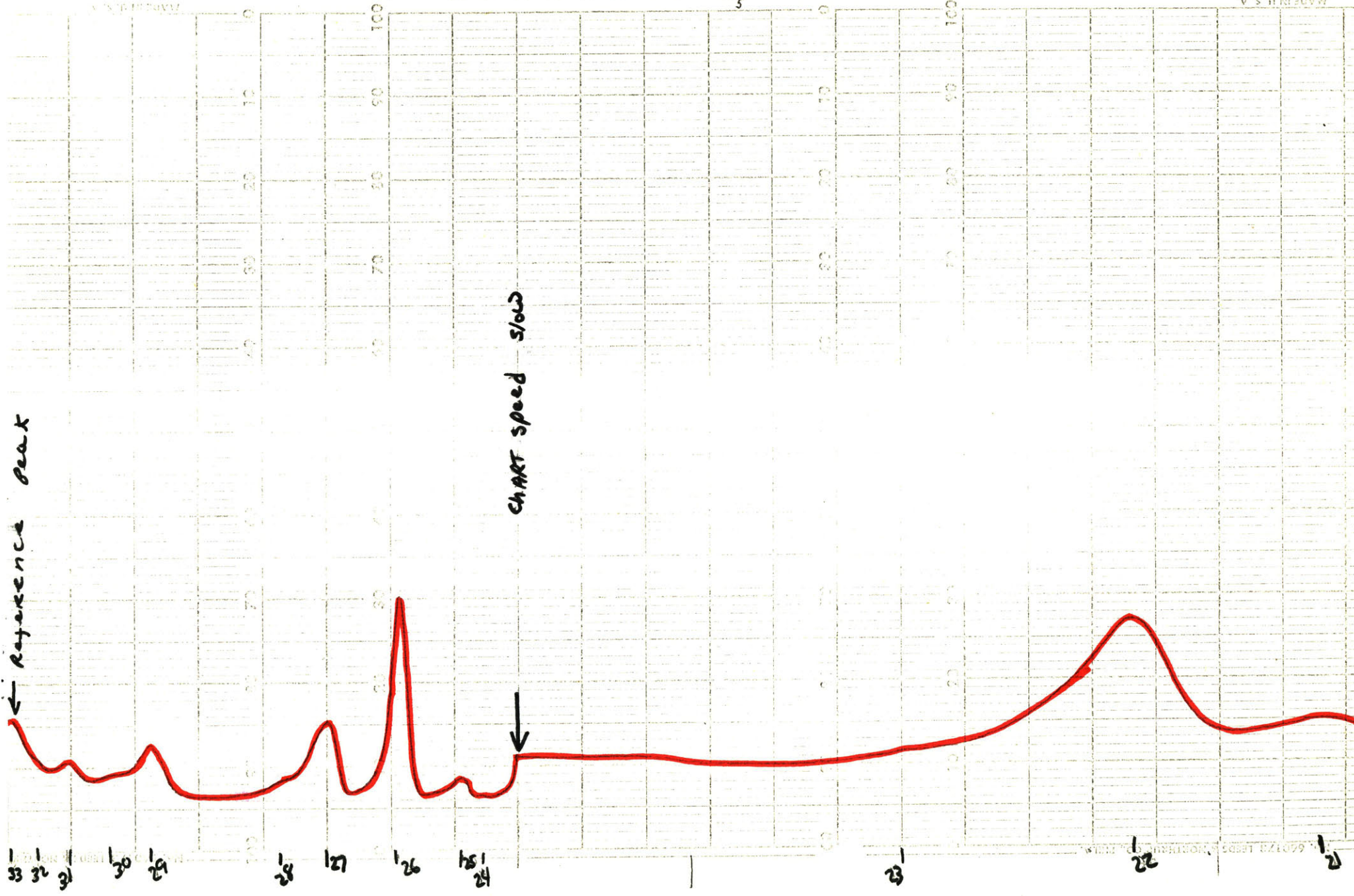
V. 2. 6. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100.



143

142

← Reference Peak

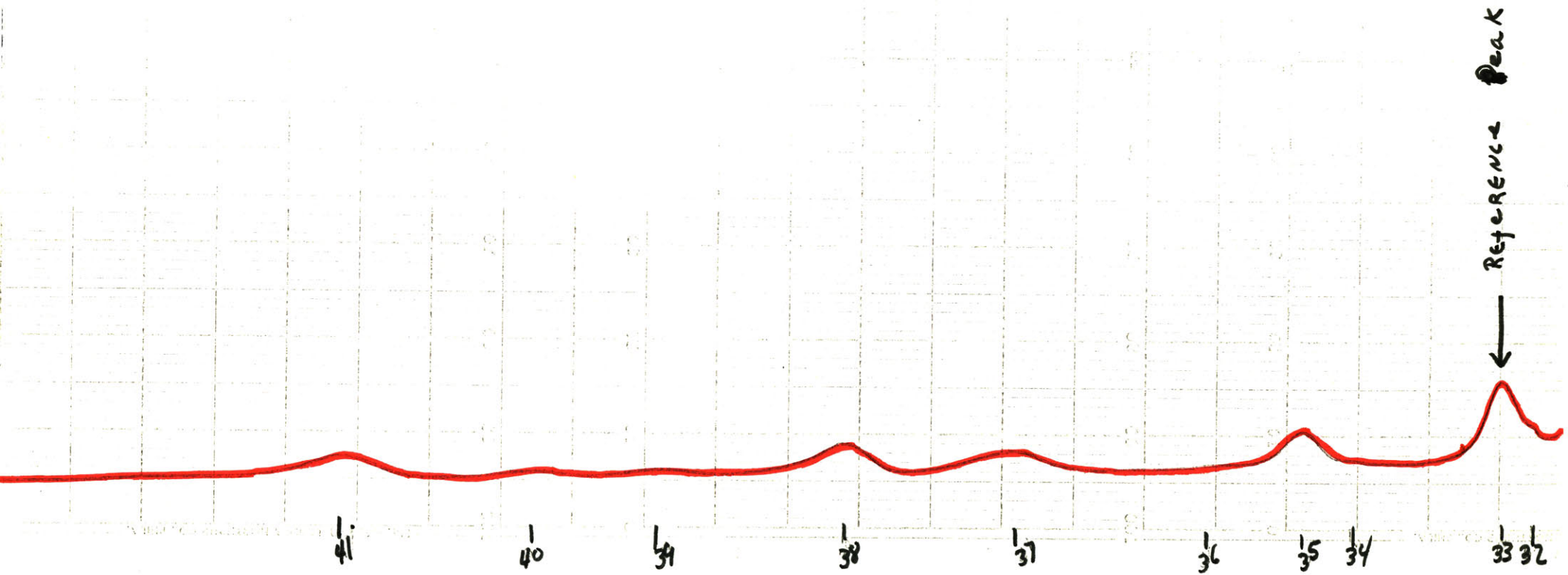


11.5

MADE IN U.S.A.

33 32 31 30 29 28 27 26 25 24 23 22 21

MAGNETIC



Chromatograph #3

Detector 210°C

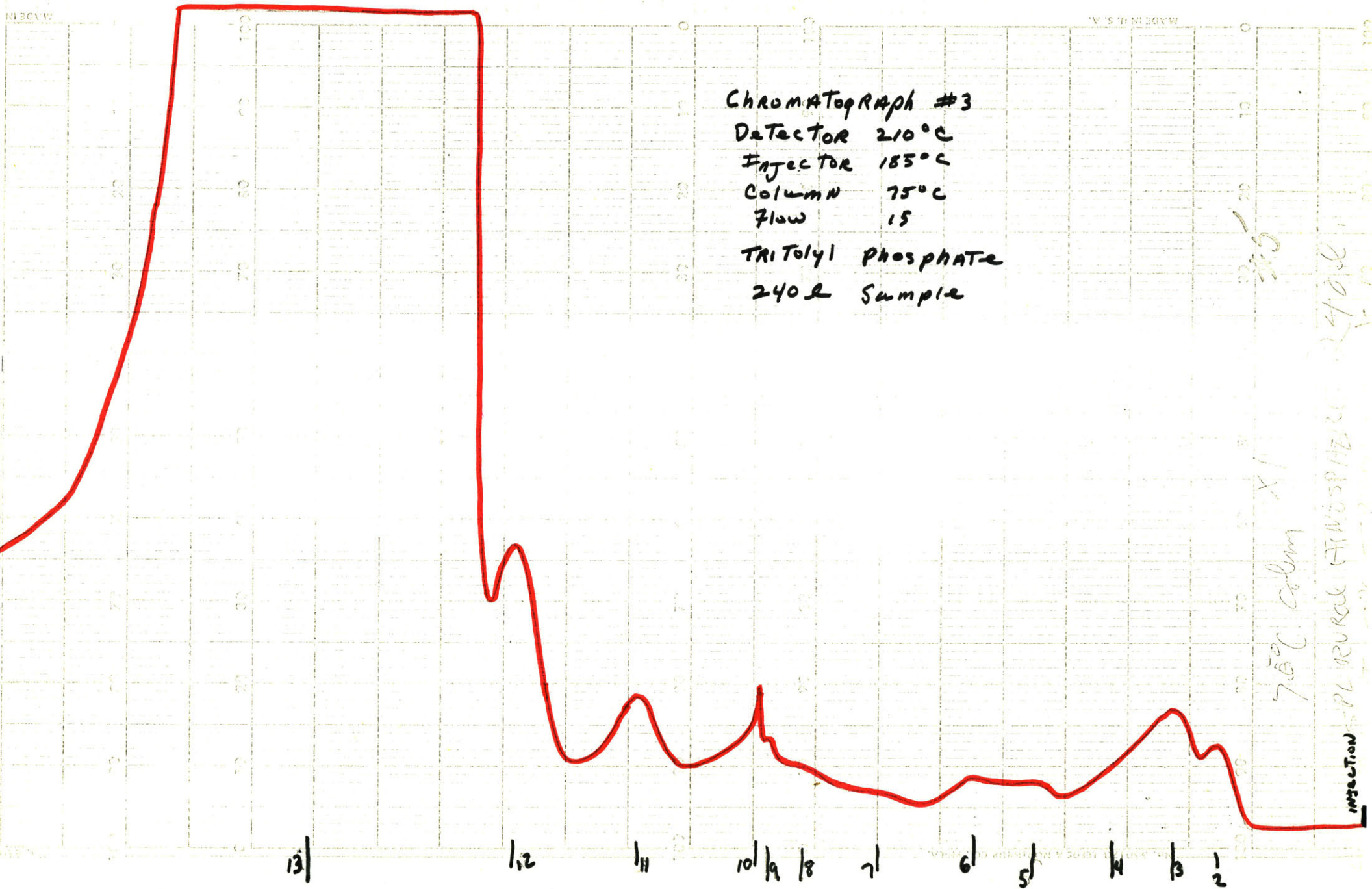
Injector 185°C

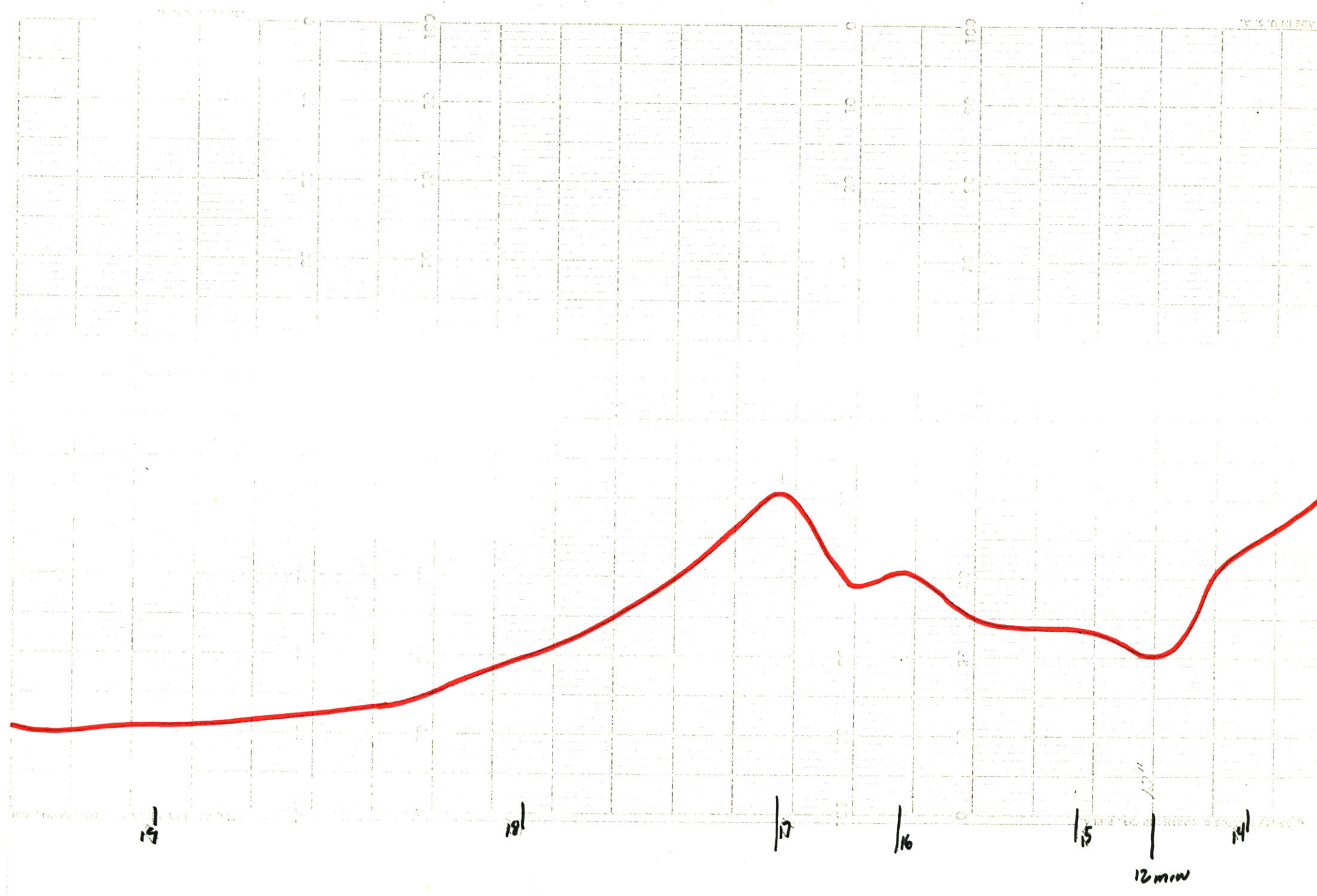
Column 75°C

Flow 15

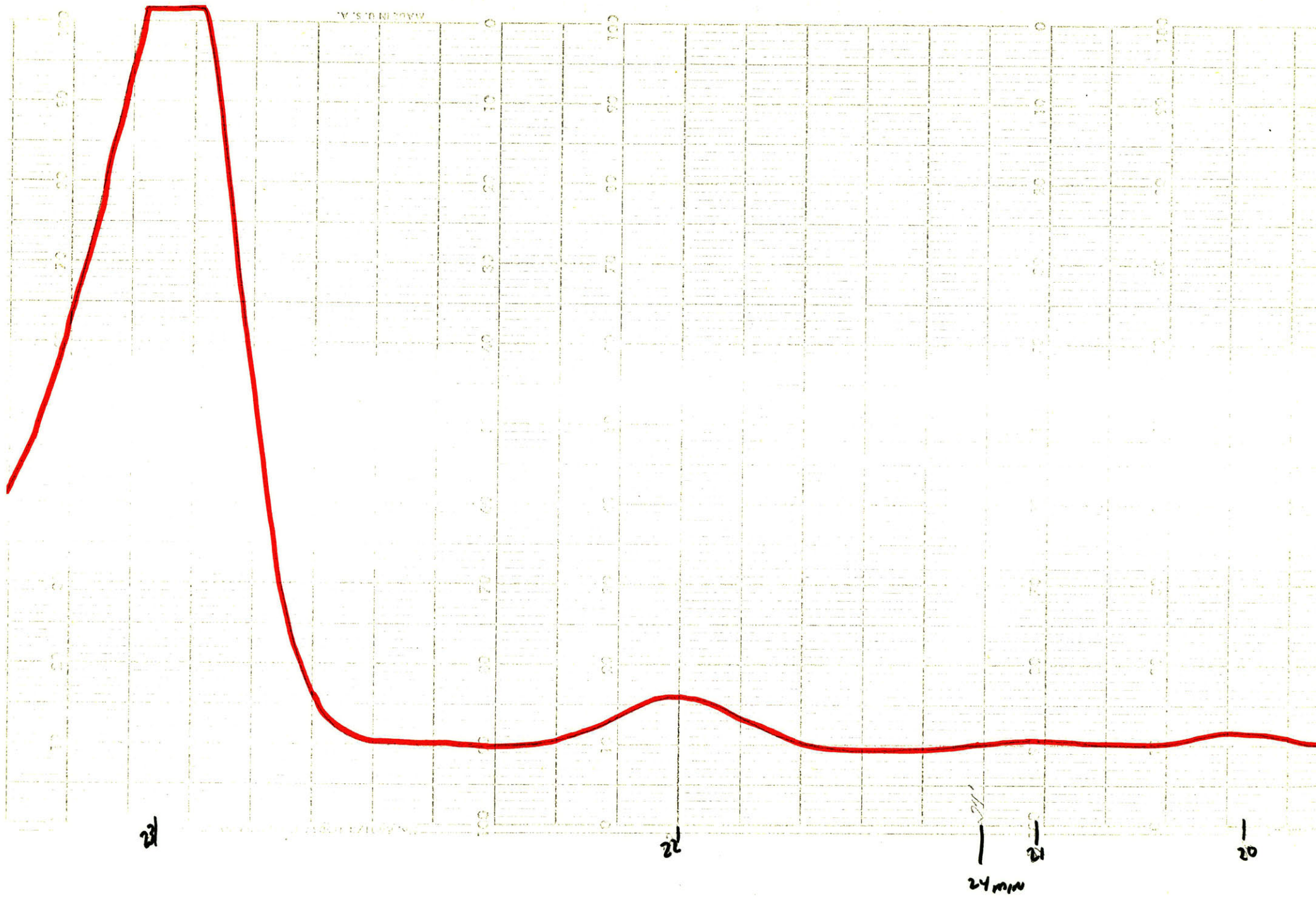
TRITOLYL PHOSPHATE

240 μ Sample





12" 12 min



MADE IN U.S.A.

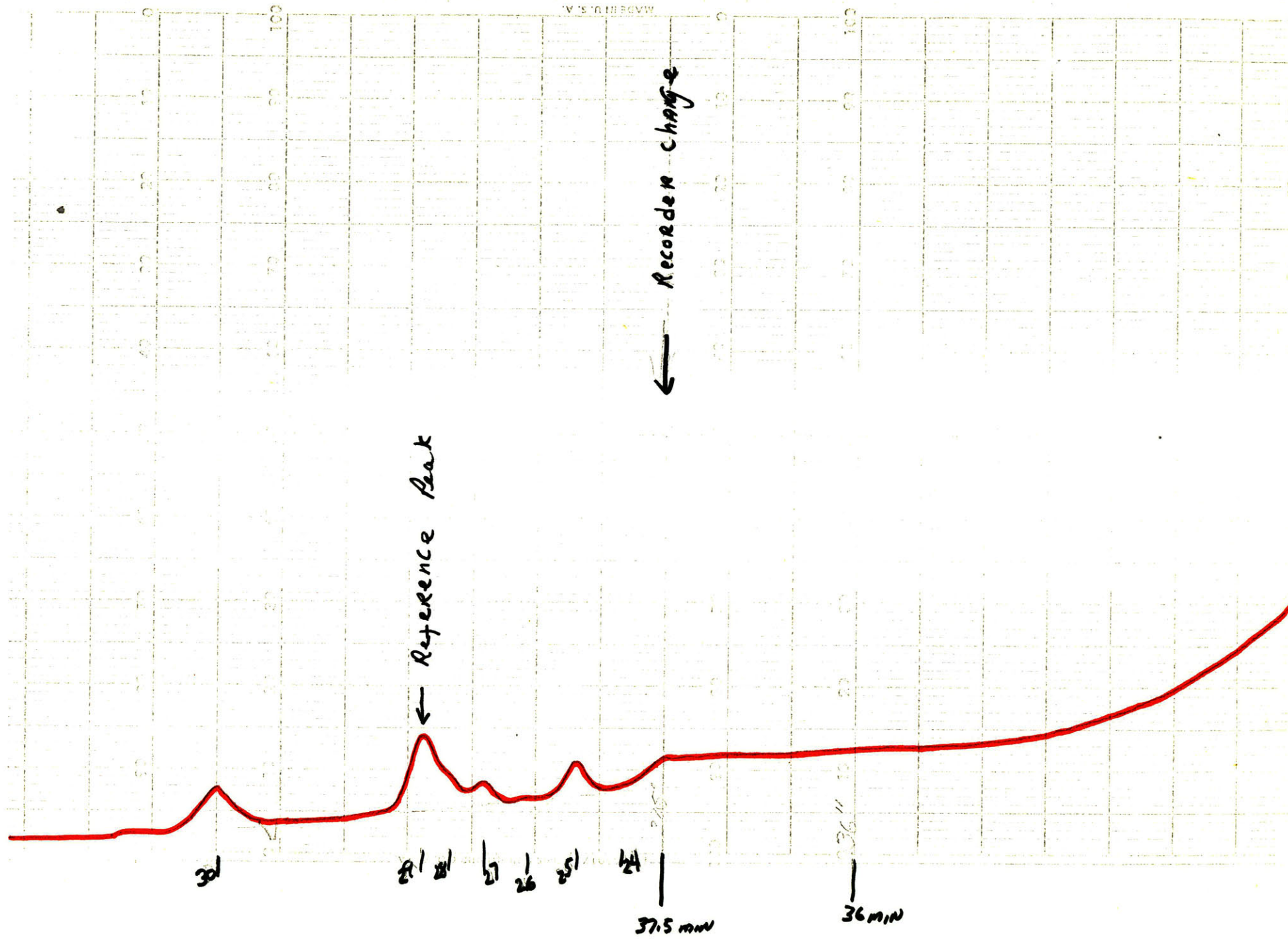
22

21

24 min

21

20



Reference Peak

Recorder change

301

281

27

26

251

24

37.5 mm

36 min

Altshuller, A. P., American Ind Hygene Ass., Vol. 23, 1962, pg. 164.

Altshuller, A. P. and Bellar, Gus "Chromatographic Analysis of Hydrocarbons in the Los Angeles Atmosphere," Air Poll. Cont. Ass., Vol 13, #2, pg. 81, 1963

Altshuller and Clemens, Gas Chromatographic Analysis of Aromatic Hydrocarbons at Atmospheric Concentrations Using Flame Ionization, Anal Chem, 34, #4, 966.

Araki, Shun and Tatsuo Kato, Tokyo Metropolitan University, Bunseki Kagaku, 11, 1962, pg. 533.

Bellar, T., Brown, Sigsley, Determination of Atmospheric Pollutants in the Part-Per-Billion Range by Gas Chromatography, Anal Chem, 35, #12, 1924.

Bellar, T., Sigsby et. al., Direct Application of Gas Chromatography to Atmospheric Pollutants, Anal Chem, 34, #7, p 763.

Brenner, N., Cieplinski, Ettore and Coates, Molecular Sieves as Subtractors in Gas Chromatographic Analysis, J. Chromatog., 3, 230.

Browning, E., Toxicity of Industrial Organic Solvents, N. Y., Chemical Publishing Co., 1953.

Farrington, P. S., Pecsok, R. L., Meeker and Olson, Detection of Trace Constituents by Gas Chromatography, Anal Chem, 31, 1512.

Fleming, R. D., B. Dimitriades and R. W. Hurn, Procedures in Sampling and Handling of Automobile Exhaust, Journal of Air Poll., Cont. Ass., Vol 15, Aug. 65, 361.

Haagen-Smit, A. J., The Control of Air Pollution, Scientific American, January 1964, pg. 25.

Hoff, J. E., Feit, E. D., Functional Group Analysis in Gas Chromatography, Anal Chem, 35, #9, 1298.

Hoff, J. E. Feit, E. D., New Technique for Functional Group Analyses in Gas Chromatograph, Anal Chem, 36, #6, 1002.

Innes, W. B., Bambrick and Andreatch, Hydrocarbon Analysis Using Differential Chemical Absorption and Flame Ionization Detection, Anal Chem, 35, #9, 1198

Lovelock, J. E., A Practical Guide to Ionisation Detectors for Chromatography, R & D, October, 1961.

Leighton, P. A., Photochemical Reactions in Contaminated Atmospheres: A Survey. Chemical Reactions in the Lower and Upper Atmosphere, Interscience, N. Y., 1961.

McDermott, Air Pollution and Public Health, Scientific American, p. 49, Vol. 205, no 4.

Martin, R. L., Determination of Hydrocarbon Types in Gasoline by Gas Chromatography, Anal Chem, 34, #8, 896.

Merritt, C., Jr., Walsh, J. T., Qualitative Gas Chromatographic Analyses by Means of Retention, Volume Constants, Anal Chem, 34, #8, 903.

Parcher, J. F., Urone, P., An Improved Solution Coating Technique for Gas Chromatographic Supports, p. 184, Journal of Gas Chromatography, June, 1964.

Purnell, Howard, Gas Chromatography, John Wiley & Sons, New York, 1962.

Ross, A. H., Smith, et. al., Comparison of Auto Exhaust Emission in 2 Major Cities, Journal, Air Poll. Cont. Ass., 15, Aug 65, 362.

Rowan, R., Identification of Hydrocarbon Peaks in Gas Chromatography by Sequential Application of Class Reactions, Anal Chem, 33, 658

Smith, M. E., The Concentrations and Residence Times of Pollutants in the Atmosphere., Chem Rx's in the Lower and Upper Atmosphere, Interscience, New York, 1961.

Stephens, E. R., The Photochemical Olfine-Nitrogen Oxides Reaction, Chemical Reactions in the Lower and Upper Atmosphere, Interscience, N. Y., 1961, pg. 51

Suffis, R, and Dean, D. E., Identification of Alcohol Peaks in Gas Chromatography by Nonaqueous Extraction Methods, Anal Chem, 34, #4, 480.

Sutton, O. G., Micrometeorology: A Study of Physical Processes in the Lowest Layers of the Earth's Atmosphere, McGraw Hill Book Co., Inc., 1953.

Sutton, Sir Graham, Micrometeorology, Scientific American, Oct, 1964, Vol 211, No. 4, p. 62.

Tuesday, C. S., The Atmospheric Photooxidation of Trans-Butene-2 and Nitric Oxide, Chem Reactions in the Lower and Upper Atmosphere, Interscience, New York, pg. 15, 1961.

Wayne, S. G., Romanousky, J. C., Rates of Reaction of the Oxides of Nitrogen in Photo-oxidation of Diluted Automobile Exhaust Gases., Chem Rx's in the Lower and Uppers Atmosphere, Interscience, New York, 1961, p. 71.

West, P. W., Sen, B, Sant, Mallik, and Sen Gupta, Journal Chromatography, 6, 220.

Williams, F. H., Gas Chromatographic Techniques for the Identification of Low Concentrations of Atmospheric Pollutants, Anal Chem, 37, 1723.