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GAS CHROMATOGRAPHIC ANALYSIS OF CURING SMOKES

(A Progress Repórt)

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(with 3 figs.)

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Introduction

During the VIIth Conference of Meat Research Institutes (1961) the results of preliminary experiments in gas chromatographic analysis of curing smokes were presented (1).

For further work on the same subject the Griffin M2B VPC Apparatus was additionally equipped in our Department for programmed temperature operation. Nevertheless the analytical results could not be significantly improved. It became clear that the great number of chemical compounds present in the curing smoke cannot be directly separated (without any chemical pretreatment) and detected with this type of chromatograph. The idea of direct introduction of the smoke samples onto the top of the analytical column could not be realized with good results using this type of apparatus, too.

In further experiments in which only ether extracts of the curing smoke samples were analysed the more sensitive Pye Argon Chromatograph was used. With the help of this instrument much better results could be achieved.

Experimental

The curing smoke obtained from an amount of 30 to 60 g of beech sawdust in a laboratory smouldering-type all-glass smoke generator in constant conditions was trapped in ethyl ether. The ether extract of smoke components was divided into equal parts which were treated with different group reagents in order to separate the respective groups of compounds. The prepared samples were dried with anhydrous Na_2SO_4 and the solvent was removed at room temperature under vacuum in the presence of nitrogen. The

ether extracts condensed to constant volume were analysed on the Pye chromatograph.

The group reagents and processing regime applied in this experiments are listed in Table I.

The samples were introduced on the top of the column with the help of a 0.1 microliter micropipette. The columns were held under isothermal conditions at 100°, 150° and 190°. Also other temperatures were tested (125, 175°). When programmed temperature operation was applied the column was held initially at 100°; after that the temperature was raised up to 192° C. The Pye argon chromatograph was not equipped for PTGC. This caused an simultaneous rise of the base line during temperature programming. Furthermore there was only one heating rate possible.

TABLE I

Sample code	Treatment
A. or the current letter giving the number of the sample.	Untreated, dried original ethyl ether smoke solution
A-1	Original sample extracted with distilled water
A-1.1	Ether extract of the combined water portions used for the preparation of sample No. A-1
A-2	Original sample extracted with $NaHSO_3$ solution
A-2.1	Ether extract of the combined fractions of $NaHSO_3$ so . used above, after washing of the solution with ether and alkalization with Na_2CO_3
A-3	Original sample extracted with Na_2CO_3 sol.
A-3.1	Ether extract of the combined fractions of Na_2CO_3 sol., after washing with ether and acidification with H_3PO_4
A-4	Original sample extracted with NaOH sol.
A 4	Ether extract of the combined fractions of NaOH sol. after washing with ether and acidification
A-5	Original sample after reaction with dry NH_3
A-5.1	Ether extract of the ether washed and acidificated precipitate obtained at A-5.

Different column filling materials and different temperatures were tested in order to find optimum conditions for the separation of the smoke components of the untreated sample.

Results and discussion

Untreated samples of curing smoke contain a great number of compounds having different boiling points, from low boiling carbonyl compounds to very high boiling phenols and hydrocarbons. At low column temperatures only few peaks could be separated.

Using columns filled with solvents specially recommended for the analysis of phenols only very unadequate results were obtained at considerably low temperatures. Columns filled with xylenyl phosphate at 115° and 70 ml/Ar min gave in 30 minutes only 4 peaks. On columns with Apiezon L working at 225° only 13 peaks could be separated.

Columns with Carbowax MW 100 Polyethylene Glycol at 125° gave better results.

The best stationary phase for direct separation of the components present in wood smoke seems to be polyethylene glycol adipate, described in the litterature as a very efficient solvent for the separation of unesterified acids (2).

Detailed data obtained at different temperatures on columns filled with PEGA on celite are given in Table II. Some of the typical chromatograms are presented in the fig. 1, 2, and 3.

The great number of smoke components having different boiling points made it difficult to choose the optimal processing parameters for the separation of maximal number of smoke components present in the original untreated mixture. The amount of peaks separated at different temperatus from 100 to 192° ranged in all cases from about 30 up to 40. The greatest number of compounds was separated with programmed heating of the column during analysis (over 60). Detailed data are given in Table II and in the chromatograms.

Group identification of the peaks gave some preliminary results.

Among the 33 peaks separated at 150° on PEGA-column 17 have a good watersolubility. The largest part of the compounds represented by this peaks (13) seem to be free from carbonyl, acid or phenolic functional groups. Results of chromatographic analysis of the A-O, A-2, A-3 and A-4 samples indicate that among the 33 peaks 6 are formed by compounds having phenolic functional groups, 6 by acid compounds, 2 by aldehydes and ketones and 19 peaks represent neutral substances.

Chromatographic analysis of samples of original smoke as well

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TABLE II

Relative retentions of the components of the ether extract of the smouldering-type curing smoke.

No. of peak	Temperature of analysis		
	100°	150°	192°
1	0.009	0.03	0.06
2	0.030	0.06	0.10
3	0.055	0.09	0.19
4	0.074	0,11	0.33
5	0.080	0.13	0.53
6	0.086	0.16	0.65
7	0.101	0.21	0.70
8	0.127	0.23	0.82
9	0.145	0.28	1.00 phenol
10	0.192	0.35	1.12
11	0.224	0.42	1.36
12	0.236	0.52	1.72
13	0.261	0.59	2.15
14	0.282	0.68	2.40
15	0.336	0.76	2.81
16	0.392	0.87	3.40
17	0.430	1.00 phenol	4.00
18	0.478	1.14	4.50
19	0.575	1.24	4.80
20	0.649	1.48	5.30
21	0.775	1.62	5.90
22	0.835	1.84	6.80
23	0.930	2.06	8.00
24	1.00 guaiacol	2.13	9.80
25	1.15	2.54	10.00
26	1.33	2.87	13.1
27	1.43 phenol	3.20	14.1
28	1.58	3.55	15.5
29	1.68	4.06	17.9
30	2.00	4.45	18.2
31		5.10	
32		5.50	
33		6.30	
34		7.80	
35		8.25	

Parameters: 4 ft x 4 mm i.D. of 10 % polyethyleneglycol adipate on 100—120 mesh celite, argon flow rate 60 ml/min, chart speed 12 in/hr, sample size 0.1 microliter, attenuation x 1, x 3 and x 10; voltage 1750 V at 100°, 1500 V at 150 and 192°; argon inlet pressure 0.7 atm.; outlet pressure atmospheric.

Fig. 1

Fig. 3

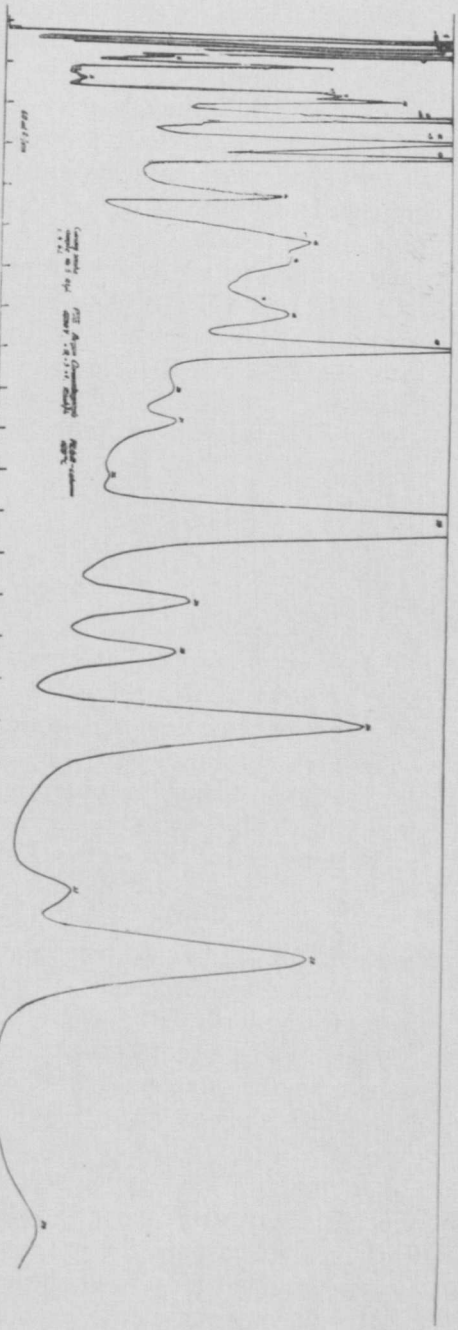

Fig. 2

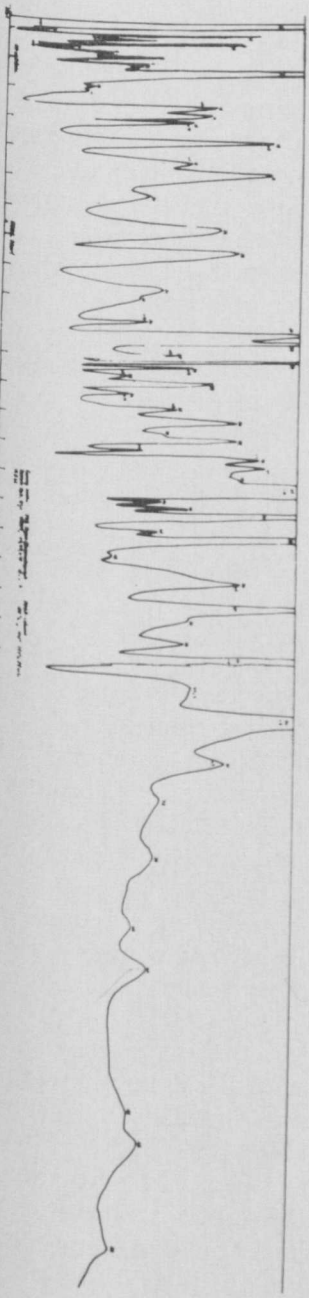

Fig. 3

as smoke treated with group reagents as given in Table I, on PEGA column at 192°, gave better results as compared with the above mentioned. Thanks to the variety of different treated samples much more individuals could be distinguished. On the B-O chromatogram 36 peaks were separated (without the first one – solvent and volatiles). Among this number 16 are composite peaks, gathered mainly in the first half of the chart; 7 peaks seem to have carbonyl functional groups, 11 react as acids and 17 as phenolic compounds. The compounds corresponding to 7 peaks, at the end of the chromatogram, did not show the presence of any of the above mentioned functional groups and could not be detected on the chromatograms B-2.1, B-3.1, B-4.1, B-4. Furthermore, 13 compounds do not show any of the functional groups but could be detected on the chromatograms B-2, B-3, and B-4, thus they are called neutral compounds of the smoke.

Detailed data are given in Table III.

Conclusions

The results indicate that direct gas chromatographic analysis of the ether extract of curing smoke can be successfully used for the separation of the compounds present in the curing smoke.

The greatest number of peaks (above 60) can be separated in about 4 hours using the programmed temperature gas chromatography method. Up to 36 peaks, representing at least 53 compounds, can be separated at 192° on the PEGA column, using argon ionization detector.

For group identification of the peaks simple group reactions can be used. Among the corresponding groups of compounds further identification can be made on the basis of retention data obtained for pure standards.

Much better results in the separation of the components of original smoke samples should be achieved using a chromatograph equipped with ionizing detector and programmed heated column oven.

For practical utilization of this direct gas chromatographic analysis of untreated curing-smoke samples (ether extracts) further work on the identification of the peaks should be carried out. After a complete identification of all peaks this method could be used for control purposes in smoke generation and smoke curing processes as well as in research work on smoke-curing phenomena.

TABLE III

Results of gas chromatographic analysis of original curing smoke ether extract and samples treated with group reagents.

Sample Number	Sample code (see Table I)								Preliminary*) identification			
	B-0	B-2.1	B-2	B-3.1	B-3	B-4.1	B-4	B-5. 1				
1	+	+	+	+	+	+	+	+	solvent and valatiles			
2	+	+	+	+	+	+	+	+		c	a	
3	+	+	+		+		+			c		
4	+	+	+	+	+	+				c	a	
5	+		+	+	+	+	+	+	n		a	
6	+		+	+	+	+	+	+	n		a	
7	+		+		+	+	+	+	n			p
8	+			+	+	+	—				a	p
9	+		+		+	+		+				p
10	+		+		+	+	+	+	n			p
11	+		+		+	+						p
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13	+		+		+	+	+		n			p
14	+		+		+	+	+	+	n			p
15	+		+		+	+	+	+	n			p
16	+	+	+	+	+	+	+			c	a	p
17	+		+	+	+	+	+	+	n		a	
18	+	+	+	+	+	+				c	a	
19	+	+	+		+	+	+	+	n			p
20	+	+	+	+	+	+	+	+		c	a	
21	+						+				?	
22	+		+		+	+	+					p
23	+		+		+	+		+				p
24	+	+			+					c		
25	+				+	+						p
26	+		+								?	
27	+		+		+	+		+				p
28	+					+						p
29	+							+			?	
30	+		+		+	+						p
31	+										?	
32	+		+								?	
33	+		+		+						?	
34	+			+		+		+			a	
35	+		+	+		+		+			a	
36	+		+								?	
37	+		+		+		+		n			

*) c. compounds with carbonyl functional group
a. compounds with acid functional group
p. compounds with phenol functional group
n. neutral compounds
?. unidentified with the help of the group reactions

Summary

It is nowadays possible, by direct gas chromatography, to separate the components of smoke as their ether extracts. The use of a chromatograph equiped with an Argon ionization detector and a programmed temperature heated oven makes it possible to obtain results of a precision unknown up to now. But the problem remains still so the control of smoke curing operation will be made possible only when all the peaks of the chromatogram have been identified.

Résumé

Il est possible actuellement, à l'aide de la chromatographie directe, en phase gazeuse, de séparer les composants de la fumée sous forme de leurs extraits à l'éther. L'emploi de chromatographes munis de détecteurs d'ionisation à Argon et de fours colonne avec chauffage à température programmée permet d'obtenir des résultats d'une précision inconnue jusqu'ici. Le problème n'est cependant pas épuisé et l'application de cette méthode au contrôle des opérations de fumage ne pourrait s'effectuer qu'après l'identification complète de tous les pics du chromatogramme.

Zusammenfassung

Mit direkter Gaschromatographie kann man heute die Bestandteile des Gazes in Form ihrer aetherischen Auszüge trennen. Die Verwendung des Argon-Ionisationsdetektors und eines temperaturprogrammierten Säulenofens verleiht dem gaschromatographischen Verfahren eine bisher unerreichte Genauigkeit. Die Untersuchung auf diesem Gebiete sind jedoch nicht abgeschlossen. Die Anwendung dieses Verfahrens zur Kontrolle der Verdampfungsvorgänge kann erst vorgenommen werden, wenn sämtliche Chromatogrammspitzen identifiziert sind.

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2. Pye Separation Techniques No. 8.

tive and quantitative data on the composition of the main groups of smoke components.

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Experiments.

In order to overcome both difficulties an attempt was made to apply the gas chromatographic method in smoke analysis.

In the first approach gas chromatography was applied to the analysis of the main groups of compounds, isolated from the original mixture/ smoke condensate /.

In all experiments the Griffin Mark 2B Apparatus was used with hot wire detector, and column fillings stable in temperatures up to 200°C.

Data regarding the composition of the carbonyl compounds group have been presented at the Gdańsk's Session. / 3 /. Five components have been found: furfuralehyde ~ 47 %, acetone - 23 %, benzaldehyde 11 %, valeric aldehyde 2 % and one unknown.

The acids isolated from the original smoke condensate were separated on silicone elastomer column, using the trans-esterification method proposed by J.N.Ralls / 5 /. A special reactor was made instead of the capillary used by Ralls and the reaction was carried out in the carrier gas stream.

Five acids were found, i.e. acetic acid / 66%/, formic acid / 29%/, propionic acid /4%/ and two unknown still unidentified. The last two present in traces could not be detected in the original untreated mixture of sodium salts and were found when the major part of the 3 foregoing acids has been removed from the mixture.

Typical chromatograms obtained in both analyses are shown in firure No.2.

Preliminary analysis of the phenolic fraction of the curing smoke resulted in chromatograms showing only one main component. This indicates that similiarly as in the case of

acids , an enrichment of the trace components is necessary. 355

In further experiments th problem of smoke sampling was attacked. According to the opinion of K.Miler / 6 / the ideal smoke sampling procedure should be the dir ct introduction of smoke on top of the chromatographic column. This avoids any undesirable reactions between the components and any loss of constituents during the pretreatment.

Attempts were made to realize this idea. The general arrangement of the apparatus used in the experiments is shown in fig. No.3.

During the period of smoke generation the chromatographic column was held at ambient temperature. The organic smoke constituents dissolved in the column liquid and during the 1 to 5 minutes of sampling did not move far enough to cause any considerable overlapping and peak distortions. Subsequently the programmed temperature operation was applied. Unfortunately our chromatograph is not provided with separate chambers for the detector and columns and the base-line had therefore great long term drift. Nevertheless the peaks resulting during elution of components could be clearly distinguished.

Conclusions.

The direct introduction of curing smoke on gas chromatographic columns and the subsequent programmed temperature gas chromatographic separation of the components of the original mixture seems to be a valuable method for the determination of the individual main smoke constituents. The best column filling materials and working parameters for the analysis of such complex mixtures should be found in order to improve this technique.

Class reaction should be used for the identification of the peaks resulting in chromatograms instead of using this reactions to separate the main groups of compounds from the origi-

nal mixture prior to chrometographic analysis.

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Zusammenfassung

Gas chromatographische Methoden wurden in der Rauchrauch-Analyse angewendet. Es wurden die Hauptkomponente der einzelnen Gruppen von Verbindungen / Sauren, Karbonyl-Verbindungen / bestimmt. Auch wurden Versuche durchgefuehrt, in denen der Rauchrauch direkt auf den Verteilungskolonnen abgesetzt und anschliessend bei kontinuierlicher Erwarmung chromatographiert wurde.

Streszczenie.

Zastosowano metody chromatografii gazowej do oznaczenia składników głównych grup związków wyodrębnionych z dymu wędzarniczego. Przeprowadzono także próby bezpośredniego wprowadzenia dymu na kolumny chromatograficzne i rozdziału składników przy programowym ogrzewaniu w czasie analizy.

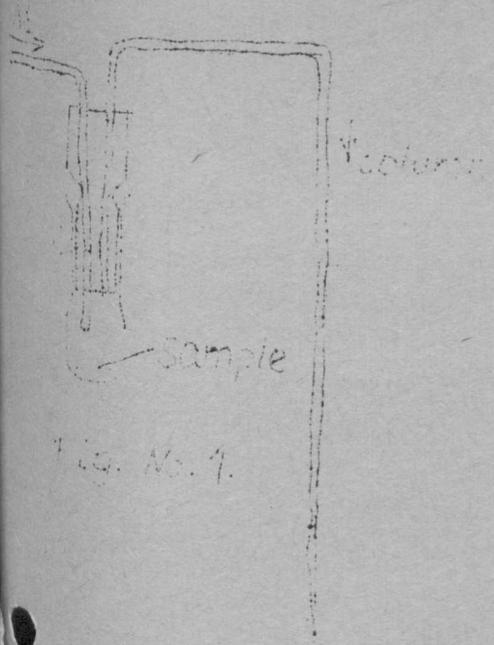

Fig. No. 1.

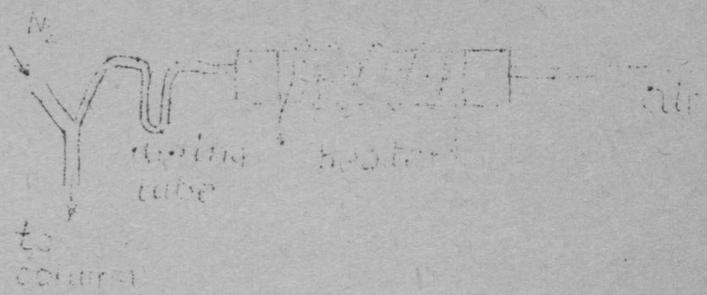

Fig No. 3

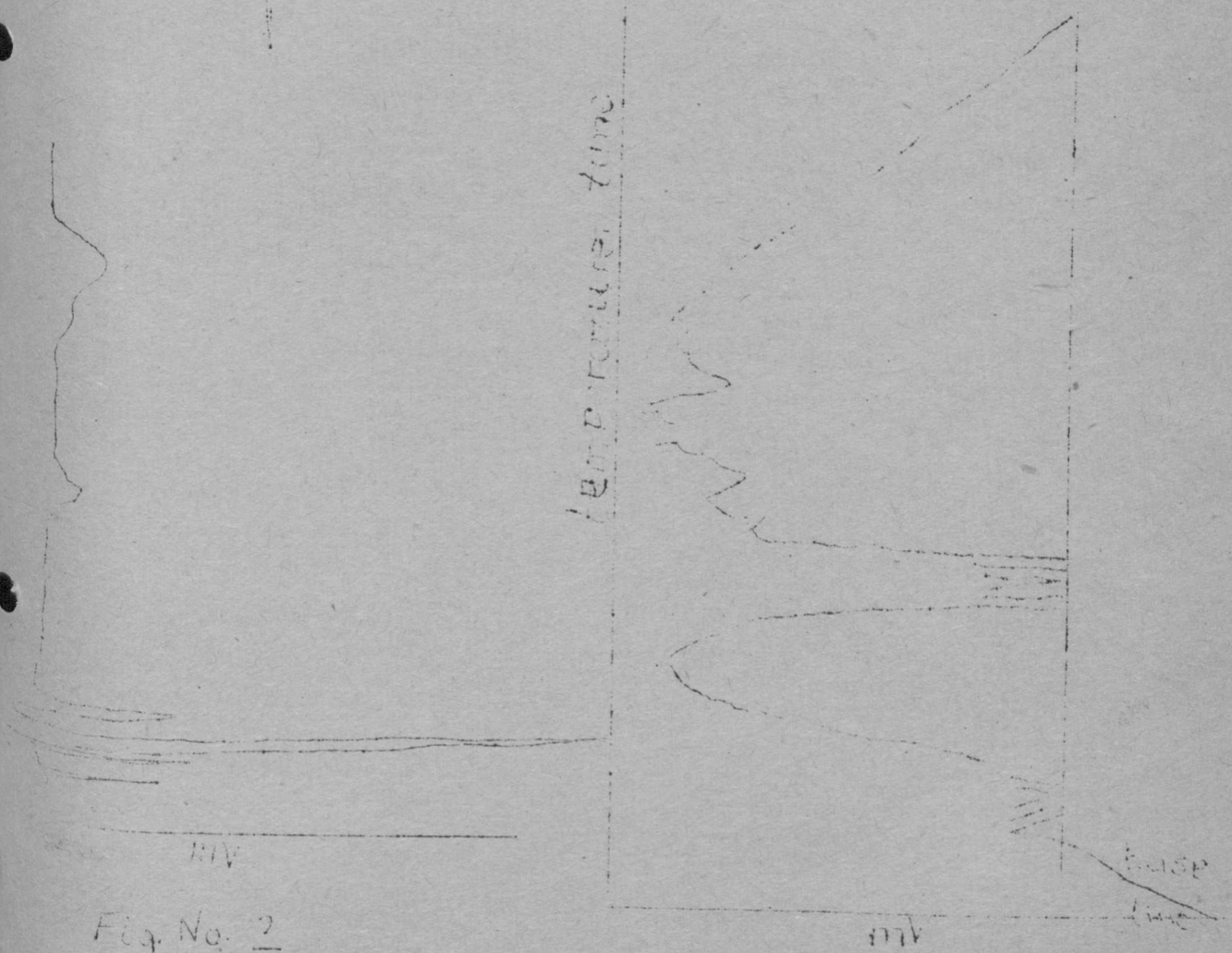

Fig. No. 2

Fig. No. 4