

DEVELOPMENT OF A CARBON CARRIER FOR OLIGODYNAMICALLY ACTIVE SILVER

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## SUMMARY

A carbon carrier for silver has been developed to act as a source of silver ions useful for disinfection in oligodynamic concentrations (0.05-1.0 parts per million).

A certain type of carbon, consisting mostly of lampblack, was found to fulfill the necessary conditions of electrical conductivity and high electrolytic adsorption. This material, in the form of small, hard cylinders, is impregnated with silver by soaking in a 10 percent silver nitrate solution for a few minutes. After air drying, the carbon is heated in a muffle furnace to reduce the silver to metallic form, finely dispersed throughout the body of the carrier. The carbon silver carrier is then given an anodic electrolytic treatment, charging with 90 coulombs per 1.6 gm. carrier at a current density of about 7 ma./cm.<sup>2</sup> for 30 minutes. After charging, the carrier is carefully rinsed in distilled water and air dried.

Although the process by which the silver ions are emitted from the carrier is of an oxidation nature, the complete mechanism is not yet entirely understood. The electrolytic treatment gives the carrier the property of emitting silver when immersed in water. The silver emission, which is germicidally active, declines exponentially with the time, giving approximately 5 mg. in 90 minutes, and is complete within a few hours. The prepared carrier is unaffected by heat even with a 1 hour exposure to 350° C., and retains its activity over periods of more than a year, whether wrapped in cellophane, paper, or sealed in dry air or vacuum.

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## I. INTRODUCTION

### A. The Oligodynamic Action of Metals.

A writer on medical subjects in Sanskrit of 2000 B. C. said: "It is good to keep water in copper vessels, to expose it to the sunlight, and to filter it through charcoal." (1) The Egyptians apparently used silver plates to cover open wounds to cause more rapid healing, (2) and Cyrus, on an expedition, stored his water in silver containers. (3) Nägeli (4), however, made the first careful modern investigation of the effects of low concentrations of metals and their salts, and reported the growth-hindering and killing effect on algae. The word oligodynamic was coined by Nägeli to denote the power of a small number, thus an oligodynamic substance is one "effective in small quantities" (5) in disinfection. This may be defined to mean the range of concentrations below 1 milligram per liter.

The literature covering the research in oligodynamics includes several hundred papers and scores of patents. Summaries of work with the various metals, and their applications under a wide range of conditions, with extensive bibliographies, are given by Saxl (6), Siebeneicher (7), Raadsveld (2), and Goetz, Tracy and Harris (8). Though disinfection of many liquids has been investigated, the principal use is in sanitizing water. The concentration of silver necessary to disinfect water in two hours, contaminated with non-sporulating bacteria, is agreed (8), to be in the range 50-500  $\gamma$ /liter. (1 $\gamma$  = 1 microgram)

### B. Methods of Activating Silver for Oligodynamic Purposes.

Many types of methods have been utilized to produce a sufficient

concentration of silver ions in the water to be disinfected. It is now generally agreed that the active agent is the silver ion, though the mechanism of the biological action is not understood. Since metallic silver is only soluble to about 25-35  $\mu$ /liter, even with long exposure to water (9) (10), it is necessary to activate the silver in some manner to get more silver ions available. Examples, taken from the patent literature, of different kinds of methods include: Heat silver salts or gels in oxidizing or reducing atmosphere (11); a silver coated material subjected to "corroding" material such as ozone or chlorine (12); two metals connected together with or without additional potential, one metal being more electropositive than hydrogen, the other less (13); electrolysis or current between silver or platinum electrodes through a sodium chloride solution (12); activation of a metallized carrier by making it anode (12); impregnating a filter by precipitating silver chloride, arranged so that the silver and chlorine ions meet in the filter (14); reducing silver where it can be absorbed by suspensoids such as clay or subdivided carbon (15); coating a material with silver by reducing silver compounds (16); clinker macerated in silver nitrate, the reaction forming silver hydroxide, then the clinker made into filters (17); zeolite and silver nitrate, using partial base exchange reactions and reactivation with sodium chloride (18); oxidizing silver to an oxide with a permanganate (19); using hydrogen peroxide and silver (20); increasing the surface exposed so that more silver will go into the liquid (21); using an electric current between silver electrodes in the liquid to be sterilized (22). On the last method, "Uniform distribution would seem to be the only advantage over adding silver nitrate." (23) For other patents see (7)(9).

## II. CARRIERS FOR THE OLIGODYNAMIC METAL

Several types of carrier materials have been tested. Examples of such materials tested are silica gel, nephrite, charcoal and lampblack. In addition, three commercial products, used as sources of silver, were tested, "Katadyn" on ceramic beads and gravel, and "Syngasept," which is a silver-manganese dioxide on pumice carrier.

The Katadyn beads, perhaps because they were old, were very poor sources of silver. The Katadyn gravel seemed to have an upper limit of a silver concentration of  $1\frac{1}{2}$ /cc. approximately, when used in a quantity of say, 30 gms. in 10 cc. for  $1\frac{1}{2}$  hr., or in 200 cc. of distilled water for many hours. 1.3 gm. in 200 cc. in 7 days gave off a total of 1.5 mg. Ag. Large quantities of the gravel have to be used or a long time since the emission is slow but lasts a long time. The long life was shown by changing the emission water many times and the silver concentration still reaching the equilibrium value.

The Syngasept gave, in a typical test, 1 gm. in  $3\frac{1}{2}$  hr. a total of .015 gm Ag emission in 10 cc.; 1 gm. in 250 cc. in 12 hrs. gave a total of .0375 mg.; while 1.3 gm. in 200 cc. in 7 days gave a total of .9 mg.

Nephrite was tried because it is an inert porous material. It was unsatisfactory because of the extremely small silver emission.

Silica gel and charcoal have good adsorptive properties (24)(25), and might be thought desirable on that account. If they were to be used merely as carriers for a solution of a silver salt this would be

satisfactory, but to be activated when the silver is in reduced form, a chemical treatment of some sort must be used (see patents). With silver alone, in reduced form, one test found that .5 gm. silver crystals in 10 cc. water in 4 days gave off only .0039 mg. Ag, but, treated with hydrogen peroxide, in 1/2 hr. 2.5 mg. of silver had gone into solution.

There is a material which not only has these adsorptive properties, but also is an electrical conductor, which makes available electrolytic processes to activate the silver. Attempts to charge other carriers than carbon, which is a conductor, were, of course, unsuccessful. A piece of charcoal had a resistance of 30 megohms compared to a piece of carbon (W3B) with 3 ohms.

It follows from the above discussion that the two properties which make carbon desirable for investigation are its adsorptive qualities and its electrical conductivity.

## III. DETERMINATION OF SILVER

A. Methods Available.

Much of the early confusion in the oligodynamics of silver arose from the inability to detect or measure the amounts of silver giving the effect (2). There are now available a great many tests for silver which can measure the small amounts characteristic of oligodynamic activities. The following methods have been used by various workers:

1. A colorimetric test with p-dimethylaminobenzalrhodanine, with a sensitivity of 1 part in  $5 \times 10^6$ , or 20  $\mu$ /liter (Feigl (26), Kolthoff (27)); a modification of this test employing adsorption on a collodion membrane is sensitive to 1 part in  $4 \times 10^7$  (Ettisch and Tamchyna (28)). The procedure developed at the Bureau of Standards gives a direct test in the range from 60 to 9000  $\mu$ /liter (Schoonover (29)).

2. A colorimetric test with pure methylene blue reduced to the leuco-compound of sodium formaldehyde-sulfoxylate (Schumacher (30)).

3. A colorimetric method based on the formation of red silver chromate. It is suitable for determining 25  $\mu$  of silver (Krainick (31)).

4. Potentiometric methods which are sensitive to about 1 part in  $10^8$  (Krause (32), Kr̄epelka and Toul (9), Hosenfeld (33)).

5. After concentrating in the water by suitable means, the silver is removed electrolytically from an alkaline bath and finally determined volumetrically with .001 N iodide solution, using rhodanine as an indicator (Egg (34)).

6. Nephelometric methods (Kr̄epelka and Toul (9), Kul'shiĭ and

Mutilino (35), and Hahn (36)). The method of Hahn is a nephelometric measurement based on a redox reaction using mercuric chloride and sodium hypophosphite, and measures down to 1  $\mu$ /liter.

7. Haber's method of adsorption of the silver on PbS and determining the amount by fire assay (Freundlich and Söllner (10)).

For references to other methods see (29).

It may be noted that the potentiometric methods measure the silver ion concentration, and the other methods determine the total silver present.

The rhodanine test was selected because of its simplicity, accuracy and rapid manipulation for determining small concentrations of silver in water. (29)

#### B. The Rhodanine Test. Procedure and Precautions.

As a quantitative test for silver, the colorimetric determination with p-dimethylaminobenzalrhodanine developed by Feigl (26) (cf. (27)) was used. The procedure of Schoonover (29) was followed with slight modifications.

The procedure is as follows: To a 9.5 cc. sample of the unknown, whose silver content is to be determined, add .5 cc. of 4 N  $\text{HNO}_3$  to make a total volume of 10 cc. After shaking, .6cc. of saturated alcoholic solution of p-dimethylaminobenzalrhodanine is added and the solution again shaken. After half an hour comparison is made with standards of known silver content, made by dilution from a stock silver nitrate solution.

Enough p-dimethylaminobenzalrhodanine is dissolved in 95 percent

ethyl, 5 percent methyl alcohol to make a saturated solution (0.02 percent). It was found that using .6 cc. instead of .3 cc. rhodanine, there was less of the occasional change from the normal pink or red color to an off-color (see below). The amount of rhodanine used places a limit on the useful range which can be measured, thus, if the concentration was more than about 1.4  $\gamma$ /cc. the exact amount was not easy to estimate so that in practice the unknown was diluted until a comparison could be made in the range less than 1.4  $\gamma$ /cc. Though a colorimeter was used at first, this was later abandoned for direct visual comparison, to save time, and since an accuracy of about 5 percent was sufficient. For accurate comparisons, fresh standards were made each day, since in about two days the color may give an apparent smaller concentration of about 10 percent, or more, the higher standards tend to flocculate into a precipitate and the lower standards to fade.

#### Precautions.

If the acid is not added, an orange color develops when the rhodanine is added, with or without the presence of silver. If the acid is added later the orange color weakens and becomes yellow, hence the importance of the right order in adding the reagents. If twice as much acid is added, the apparent concentration of silver is about half the real amount.

With a concentration of 1  $\gamma$ /cc. Ag, the color is not appreciably changed by concentrations of  $H_2SO_4$  smaller than 0.1 percent. Above this concentration of  $H_2SO_4$  the color is decreased. Schoonover (29) reported that a very small amount of  $H_2SO_4$  increases the depth of the rhodanine color.



With a concentration of of 1  $\gamma$ /cc. Ag the color is not appreciably changed by a  $\text{Cl}^-$  concentration smaller than 0.6  $\gamma$ /cc., whether from HCl or NaCl. Above this concentration  $\text{Cl}^-$  decreases the color. Tap water had no color when tested. Copper ( $\text{CuSO}_4$ ), mercury ( $\text{HgCl}_2$ ), and lead ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) in a concentration of 1  $\gamma$ /cc. gave no color, except the mercury with a very faint pink too weak to be measurable. With manganese nitrate 20  $\gamma$ /cc. Mn did not affect the test for 1  $\gamma$ /cc Ag, nor did a 1 percent solution interfere though it seemed to be lighter in color. A gold 1  $\gamma$ /cc. shows the same color as .3  $\gamma$ /cc. Ag. Soaking 2 mm length of fine copper wire for 2 hours in a 1  $\gamma$ /cc. Ag solution reduced the concentration of Ag in a solution by 20 percent.

Pyrex test tubes were used and after washing with tap water, they were cleaned with conc. sulfuric acid-potassium dichromate cleaning solution, rinsed with water and boiled in distilled water. Moisture-proof cellophane was used to cover the corks. Rubber stoppers were unsatisfactory. These precautions, with the change in the quantity of rhodanine practically eliminated an occasional capricious change to an off-color orange or yellow, which appearing on standing, varying from a half-hour to a day. The cause for this color change was never isolated, but the procedure above seemed to almost eliminate it. Pyrex tubes were recommended (29), but soft glass tubes, given the same cleaning treatment were also found to be satisfactory. The pipettes were also cleaned with chromic acid solution. The carbon samples were first suspended in the test tubes containing 10 cc. distilled water by an enameled copper wire, but it was discovered that when the enamel had been scrapped off, exposing a small area of bare copper, the copper replaced the silver in a concentrated silver solution (100  $\gamma$ /cc.) sufficiently to form a small silver crystal at the exposed point. Silk threads were then used.

#### IV. PREPARATION AND PROPERTIES OF THE CARBON SILVER CARRIER

##### A. The Preparation.

The standard treatment developed employed a carbon (W3B) with high lampblack content, low temperature final bake in manufacturing and made wettable. This carbon is soaked in a hot 10 percent silver nitrate solution for 10 minutes, allowed to air dry on a paper towel, and then to reduce the silver is heated in a covered crucible in a muffle furnace for one hour at 475° C. (See Appendix for calibration curves of muffle furnace.) The carbon is made anode in a very dilute sulfuric acid solution (.018 N) and a current of 50 milliamperes (ma.) per carbon is passed through the electrolytic cell for 30 minutes. (See Appendix for sketch of carbon holder.) After treatment the carbon is rinsed in distilled water to remove the electrolyte, etc., and allowed to air dry before use. Carbons so prepared will be referred to as "standard carbons," and show less than 10 percent variation between individuals. The development of this procedure and the conditions affecting the amount of silver emitted from this prepared carrier are discussed below.

##### 1. Lampblack and the Dependence on the Type of Carbon.

Amorphous carbon is considered by most workers to have the same type of structure as graphite, except that the crystal units are smaller. (37) As expressed by Thiele (38): "Intermediate members of this series (of forms lying between crystalline graphite at one end and amorphous carbon at the other) comprise all the transition forms of crystalline graphite, namely, amorphous graphite, graphitite,

graphitoid, retort carbon, etc., up to amorphous soot carbon: further, no sharply defined boundaries exist in this series between graphite and amorphous carbon; and X-ray diagrams show that even amorphous carbon still possesses some graphitic structure." (see also (39) (40).) This means that there are just the two crystalline forms of carbon--graphite and diamond--though Ruff (41) says that amorphous carbon forms a third.

The types of carbon tested (Table I) were made with varying amounts of lampblack (amorphous carbon) and coke. The carrier properties of the carbon improving with the increased amount of lampblack. These carbons also test differences in the manufacturing process (42), including the temperature of final baking, effect of boric acid, skin usually on carbons from extrusion die, wettability, addition of silver in the carbon dough, and a wide range of lampblack-coke content from almost pure petroleum coke to a very high lampblack content carbon, with just enough coke to serve as a binder. The carbons as indicated in the composition below are not pure carbon (43) (44) (45). The composition of W3B as given by the National Carbon Company is as follows: It is 99.8-99.9 percent carbon. The total impurities amount to .08-.17 percent, all water insoluble. Of the impurities the proportion is:

Silica	$\text{SiO}_2$	50-60 percent
Iron and Aluminium Oxides,	$\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$	25-40 percent
Calcium Oxide	$\text{CaO}$	1 percent, approx.
Mn, B, Mg		each a trace.

The ash of this carbon as obtained by heating at 600° in the muffle furnace amounts to 1.0-1.5 mg.

TABLE I

CARBON TYPES, THEIR DESIGNATION AND COMPOSITION				
Designation		Size	Composition	
		hole ; diam. x length		
Cl		8 mm.	1"	high coke content
LCl		8 mm	1"	2 parts coke, 1 part lamblack
Ll		8 mm	1"	high lamblack
W4B	yes	9 mm	1"	highest lamblack content; low temp. bake
W3B	yes	9 mm	1"	next " " "
W1A	yes	8 mm	1"	high " high "
W1B	yes	8 mm	1"	same as W1A low "
W2BC	yes	8 mm	1"	lower lamblack, contains " "
				boric acid
W2BD	yes	8 mm	1"	same as W2BC but no boric " "
				acid
W5B	no	8 mm	1"	purest petroleum coke available
				same as Cl but low in sulfur " "
N1A	yes	8 mm	1"	same as W1A but nonwetttable
N1B	yes	8 mm	1"	same as W1B but nonwetttable
W1B2	yes	8 mm	1"	same as W1B but outer skin, produced by the flow the the material through the extrusion die, removed by grinding. Centerless ground stock
W3B2	yes	9 mm	1"	same as W3B. Baked at 1000° (factory duplicate of previous laboratory lot)
W3B6	no	7 mm	1"	same as W3B except baked at 600°
S1	no	7/16"	11/8"	Impregnated at factory with ca. .43 percent Ag, about 15 mg. ratio of silver of others are with S1 taken as 1.25
SW1	no	7/16"	11/8"	same as S1 but wetttable
SAW1	no	7/16"	11/8"	same as S1 but "factory activated"
W4B	no	7/16"	1"	high lamblack
W4BS2	no	5/8"	19/16"	7x silver of S1; taking S1 as 1.25 8.75
W4BS3	no	5/8"	11/8"	10x " " ratio 12.50
W4BS4	no	5/8"	11/8"	15x " " 18.75
W4BS2A	no	5/8"	19/16"	"factory activated" W4BS2 8.75
W4BS3A	no	5/8"	11/8"	" W4BS3 12.50
W4BS4A	no	5/8"	11/8"	" W4BS4 18.75
W4BS5	no	8 mm	1"	2.00
W4BS6	no	8 mm	1"	4.00
W4BS7	no	8 mm	1"	6.00
W4BS8	no	8 mm	1"	8.00

Lampblack (powder) itself can be used as a carrier for the silver. A lampblack powder, .5 gm., charged, by holding the powder against a silver wire with a cotton sack, at 35 ma. for 10 mins. gave .24 mg. Ag in one case and .96 mg. in another sample, as against a control of .006 mg. impregnated and reduced but not electrolytic charge. This powder is so fine it is difficult to handle. 6.0 mg. Ag were given off by a 5 gm. weight of calcined lampblack given "standard treatment." The calcined lampblack is a lampblack which has been heated with some pitch or tar and then ground to 100-150 mesh.

The porosity and wettability of the carbons are important. Carbons given a treatment at the time of making to have them wettable (designated by W, non-wettable by N, or no designation) were found to reduce the variation between individual carbons given the same treatment.

The porosity measurements do not necessarily give an adequate idea of the permeability or adsorption capacity (46) of any variety of carbon. The kind of pores are important; the pores must be intercommunicating (47) to be efficient, the larger pore size (48) (49) permits more electrolytic action (50) and more oxygen adsorption (51). Oxidation increases the pore size (52). Table II shows the amounts of silver which different carbons will absorb when soaked in the same silver nitrate solution and heated at 600° to ash. Types L1, LC1 and C1 could not have the other material from the coke fraction removed even at 800°, though there is a high ash, there is actually no more silver in them, but probably less, since their silver emission of those with much coke (C) is about 1/10 that of L1. It will be noticed from Table III that those carbons which have a high emission rate absorbed 2 to 3 times more silver.

TABLE II

VARIOUS CARBONS AND THE AMOUNT OF SILVER ABSORBED			
Type	Center Hole	Weight	Total Ash
Cl	no	1.14 gm.	156.8 mg.
LCl	no	1.34	159.3
L1	no	1.12	213.0
W5B	no	1.76	193.0
W3B6	no	1.27	63.4
W3B	yes	1.63	65.4
W2BC	yes	1.40	57.0
W1B2	yes	1.19	38.9
W1A	yes	1.35	36.1
...			32.7
N1B	yes	1.26	51.1
N1A	yes	1.26	58.1
W1B <sub>1</sub>	yes	1.20	20.8
W4B	yes	1.11	19.0
			23.8
			lost
			20.0
			22.5
			25.3
			23.9
			23.2
			22.7
			35.4
			35.7
			64.0
			49.4

TABLE III

SILVER EMISSION FROM CARBONS WITH SAME PREPARATION		
Type	Emission in 90 minutes	
W2BC	2.8 mg.	2.9 mg.
W1A	2.3	2.2
W1B2	4.0	4.1
N1A	3.6	3.8
W4B	6.9	8.6
W2BC	4.7	4.8
W1B	9.5	9.5
N1B	5.4	4.0
W5B	4.6	4.5
W3B	9.0	12.0



An extensive study of the temperature of preheating before treatment and the temperature of reduction of the silver nitrate as

10 mg.

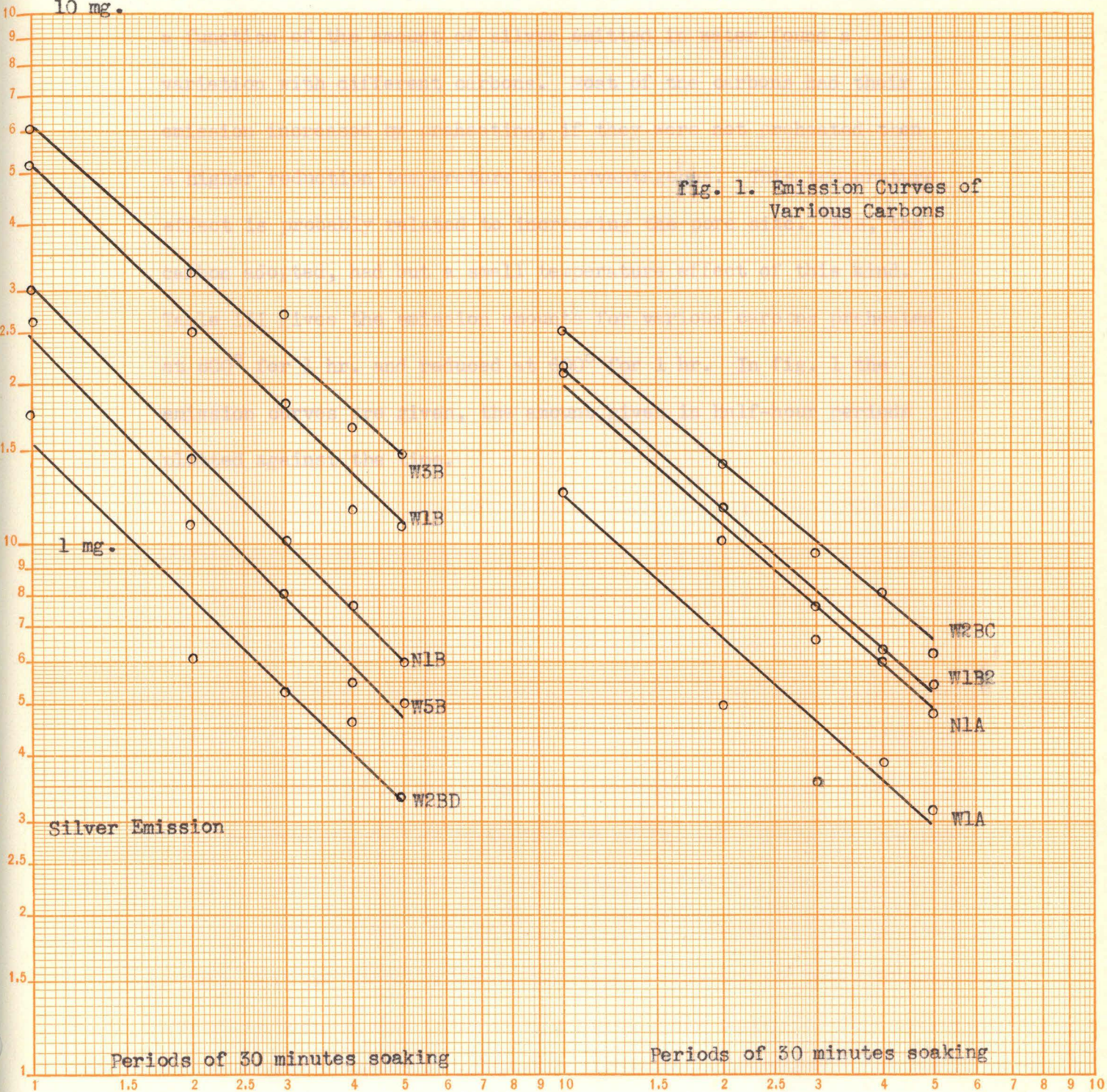
1 mg.

fig. 1. Emission Curves of Various Carbons

Silver Emission

Periods of 30 minutes soaking

Periods of 30 minutes soaking





An extensive study of the temperature of preheating before treatment and the temperature of reduction of the silver nitrate as a function of the amount of silver emitted in water found a variation with different carbons. Most of the carbons had their emission increased by preheating, if they were not preheated then a higher reduction temperature was advantageous. This temperature effect is probably related to increasing the pore size. W5B, the carbon adopted, had but a small temperature effect of this kind. Table III gives the emission amounts for various carbons preheated at  $800^{\circ}$  for 1 hr. and reduced at  $600^{\circ}$  for 1 hr. In fig. 1 the emission curves are given, the amount given in half-hour periods plotted against the time.



## A.2. Introduction of Silver into the Carrier.

The silver can be introduced into the carrier by electrolytic, chemical and physical methods. The electrolytic deposits silver on the cathode, but since only on the exterior, this is similar to using a silver sheet. The chemical method consists of soaking the carrier in a solution of a silver salt. The physical method is by mixing the carrier in powder form with silver or a silver salt.

### Chemical Method.

Silver nitrate, with its high solubility, has been found to be the most satisfactory silver salt to introduce into the carrier by soaking. Silver nitrate is the usual commercial form of silver. A high solubility is necessary since a carbon absorbs the order of 1 cc. of solution and with the less soluble salts such as silver carbonate, oxide and sulfate, not enough silver could be introduced into the carbon to be efficient. Since the amount of silver in the carbon determines the amount which can be obtained after treatment, the low-solubility silver salts were undesirable, as confirmed by tests, because of the low amounts of total silver introduced into the carbon.

The amount of silver which is soaked into the carbon seems to be a linear function of the concentration of the salt (fig. 2). The resulting activity when given a usual charge of 50 ma. for 30 minutes is also shown, as well as the emission from an unreduced though charged carbon, and the amount of residue, after soaking, from both reduced and unreduced carbons which have been charged. The amount of emission depends on the charging time and current. When 10 ma. charging current per carbon for 10 minutes was used, as study of the concentration of silver nitrate and silver emission found, this linear relation was roughly true for 0.1, 1.0, and 5.0 percent, but that 10.0 to 40.0 percent emission were about the same as 5 percent solution. There is probably an optimum

charging condition for each silver nitrate concentration. Thus if a high charge is given for a long time little silver will be left for emission and no increase in emission rate or amount is obtained. The 50 ma. for 30 mins. charge is based on a 10 percent solution. It was noticed that the silver nitrate solution tends to become more concentrated with use; a 10 percent solution which through use had been reduced to a fraction of its original volume became 35 percent. The carbons impregnated with this particular solution of silver nitrate received increasing amounts of silver as the volume of the impregnating solution decreased. This was confirmed by the emission and the silver residue after emission, and accounts for some of the variation of tests made in that period. It was found that more silver nitrate penetrated into the carbon when the carbons were soaked in a hot solution and this practice was adopted.

When the carbons are immersed in hot silver nitrate solution it is known that part of the silver nitrate is reduced by the carbon to metallic silver, and part is adsorbed as oxide and part as nitrate (62) (63) (64) (65) (67). Further evidence is the smell at the time of immersion; a smell like that of coke burning in an open grill. Probably not a large percentage is reduced since practically all the silver will come out when the carbon is soaked in distilled water, see fig. 9. With the higher coke containing carbons there is a fine sparkling surface of silver crystals on the outer carbon surface when the carrier is removed from the silver nitrate solution, they are also visible immediately after immersion (66).

A comparison test of Feigl's manganese method (53) and the electrolytic method of activation and silver nitrate gave the results shown in Table IV. Four Ll carbons were soaked in 10 percent silver

nitrate and four soaked (10 mins.) in Feigl's manner in a 40 cc. solution (2.64 gm. silver nitrate and 4 cc. of 50 percent manganese nitrate solution, made up to 40 cc.) Two samples, 1.8 gm. each of silica gel were also soaked in Feigl's solution. Two of the silver nitrate treated, two of the Feigl and one sample of silica gel were soaked 10 mins. in hot 1 N NaOH, then dried. The other samples were heated to 600° for 1 hr. and charged electrolytically. The silver nitrate carbons treated with NaOH gave an off-color rhodanine test.

#### Physical.

The mixing of silver with its carrier may be done in several ways. Mixtures of silver powder or silver salts with various oxides of cobalt, copper or manganese were not efficient, little, if any more, silver went into solution than would be expected with<sup>out</sup> the added foreign salt. Carbons with varying amounts of silver mixed in the carbon dough during the process of manufacture (see Table I where S means silver added during manufacture). The amount of silver added ranged from about 15 mg. per carbon to 340 (larger size). The amount of silver emitted increased with the silver content of the carbon, this was true whether the carriers were soaked in water as they came from the factory, or whether they were given an electrolytic activation, the latter giving an emission of 2 to 3 times more silver. Even though they had large amounts of silver already, the silver nitrate treatment gave a still greater activity. Since the amount of silver added in the dough had to be four times that added in the usual silver nitrate impregnation this scheme was abandoned.

Silver oxide is not ver soluble (20 mg./liter) but when dissolved

in a concentrated solution of ammonia, larger quantities can be imregnated into the carbon, or soaked onto the carbon powder. This may be then heated (54) to drive off the ammonia and water, at around  $100^{\circ}$ , apparently forming in transition fulminating silver (55). If then heated to still higher temperatures more silver is available in the 10 cc. test tubes of emission than at lower temperature heating, and more than the usual amount of silver oxide to be expected in 10 cc. (.2 gm). The total amount of silver emitted was independent of the volume of emission. For data on  $Ag_2O$  see Table V.

The effect obtained by mixing 50 mg. silver sulfate with 5 gm. of calcined carbon and heating to various temperatures may be seen in fig. 3. Only about one-sixth of the amount of silver present in the water in 36 hrs. was to be found when tested after two hours. Silver sulfate powder does not dissolve rapidly in water.

A small amount of silver, .24 to .87 mg. was obtained by mixing 2 gm. silver powder with 1.5 gm. calcined carbon which had been electrolytically charged. This seems to indicate either that the charged carbon can oxidize the silver ((58), see V), or that a local element may be formed between the particles of silver and lampblack able to send the silver into solution (cf. fig. 11, (57) (58) (59) (60) (9)). Since a silver wire was used as contacting electrode with the lampblack, some of the silver may be from the electrode, removed by the usual process when silver is an anode in an electrolytic cell. Thiele and Wolf (61) reported that .5 mg carbon mixed with 1 gm. silver powder had enough local element action to increase the sterile zones on inoculated agar plates.



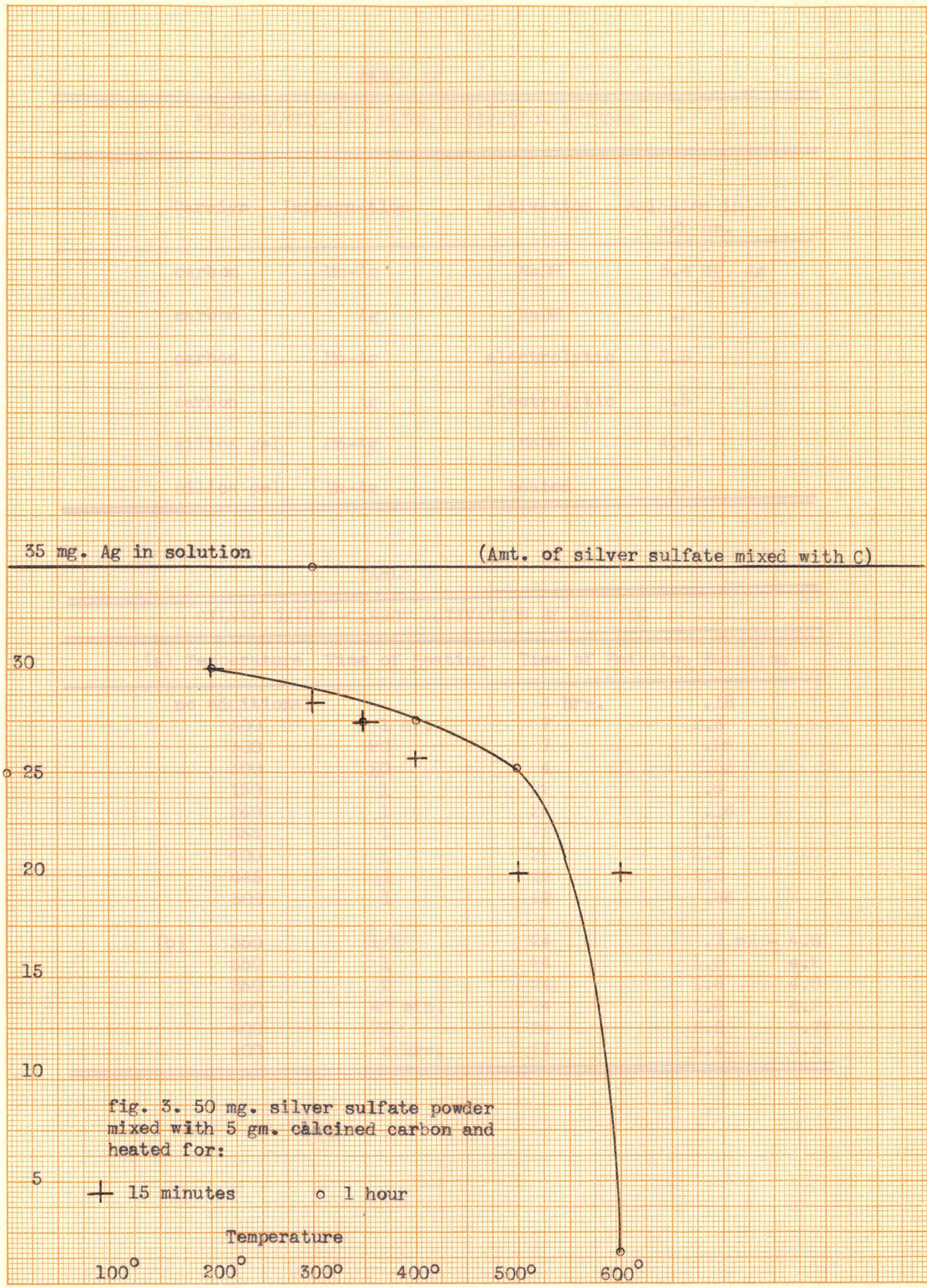




TABLE IV

ELECTROLYTIC AND WEIGL ACTIVATION METHODS			
Carrier	Impregnation	Activation	Emission in 3/2 hr.
carbon	Mn-Ag	NaOH	3.4 mg. Ag
carbon	Ag	NaOH	.2
carbon	Mn-Ag	electrolytic	3.5
carbon	Ag	electrolytic	3.5
silica gel	Mn-Ag	NaOH	4.0
silica gel	Mn-Ag	heated	.5

TABLE V

SILVER OXIDE--CARBON ACTIVATION BY HEATING			
(a) Temperature	Time of Heating	Time of Emission	Emission
no additional		4 hrs.	.18
300	1 hr.	7	2.5
300	20	7	.26
300	20	4	.33
150	1	22	.6
240	1	22	.13
355	1	22	1.1
400	1	22	2.9
445	1	22	2.0
500	1	22	.86
(b)			
350	1/2	24	.7 pH = 4.9
350	1	24	1.2 4.2
350	2	24	1.8 4.0
400	40 min.	24	1.6 4.2
400	70	24	3.5 2.7?
400	2 hrs.	24	4.4 3.3

### A.3. Reduction of Silver Salts in Carbon.

Silver salts can be decomposed by heating to various temperatures, such as the following; silver carbonate ( $218^{\circ}$ ), silver oxide ( $303^{\circ}$ ), silver nitrate ( $444^{\circ}$ ) and silver sulfate ( $1085^{\circ}$ ). The decomposition is a function of several variables, including the time, being with a more rapid rate as the temperature increases. It might be supposed that these salts will be decomposed at the same temperature when they are in the carbon, or at least in somewhat the same range. Actually, they are all reduced at about the same temperature, allowing for reaction rates. Carbon has a reducing action at the temperature it begins to oxidize (68). Silver oxide is not reduced until this point (69), and silver sulfate is likewise reduced (70), even when only mixed mechanically with calcined carbon, fig. 3. The rate is slower in the latter case since the contact between carbon and silver sulfate is not very good. The points are for 1 hr. heating and for 15 mins. See also IV B. The carbon (W3B) is completely oxidized to about a 1.0-1.5 mg. ash by heating to  $600^{\circ}$  for 12 hrs or less, this is not the case, however, with carbons containing large amounts of coke. In 60 hrs. at  $450^{\circ}$  a W3B had oxidized to 5 mg.

The reduction temperature of the silver nitrate when heated for 1 hr. did not seem to affect the amount of silver later emitted, with temperatures studied above  $420^{\circ}$ , with other lower-lambblack content carbons, the preferred reduction temperature was higher.

The formation of silver carbide is not to be expected. (41) (71)

The reduced silver is very finely dispersed throughout the carbon, there is no optical difference between the center and bottom carbons in fig. 4, the center is without silver, the lower carbon with. Fig. 5 shows a silver skeleton or coat of mail obtained by burning off the

carbon at  $600^{\circ}$  which leaves the silver in the same shape as the carbon, even to the fluting in the center hole. Figs. 6 and 7 show the surface of the coat of mail and the smallness of the crystals broken from the silver structure. Figs. 4, 5, 6, 7 are from photographs by Professor Goetz.

Although under some conditions some of the carbon can be oxidized at relatively low temperatures (72), and begins slowly at low temperatures, lower than are important in such conditions as are used to reduce silver salts, the oxidation becomes rapid enough to become important in the range  $400-450^{\circ}$  (fig. 10) (64) (37).

If the carbon is reduced at  $600^{\circ}$  for 1 hr. there is no detectable amount of silver which will be emitted from the carrier in a half-hour, but at temperatures in the range  $400-500^{\circ}$  there is about .1 mg. which can come out on soaking in water.



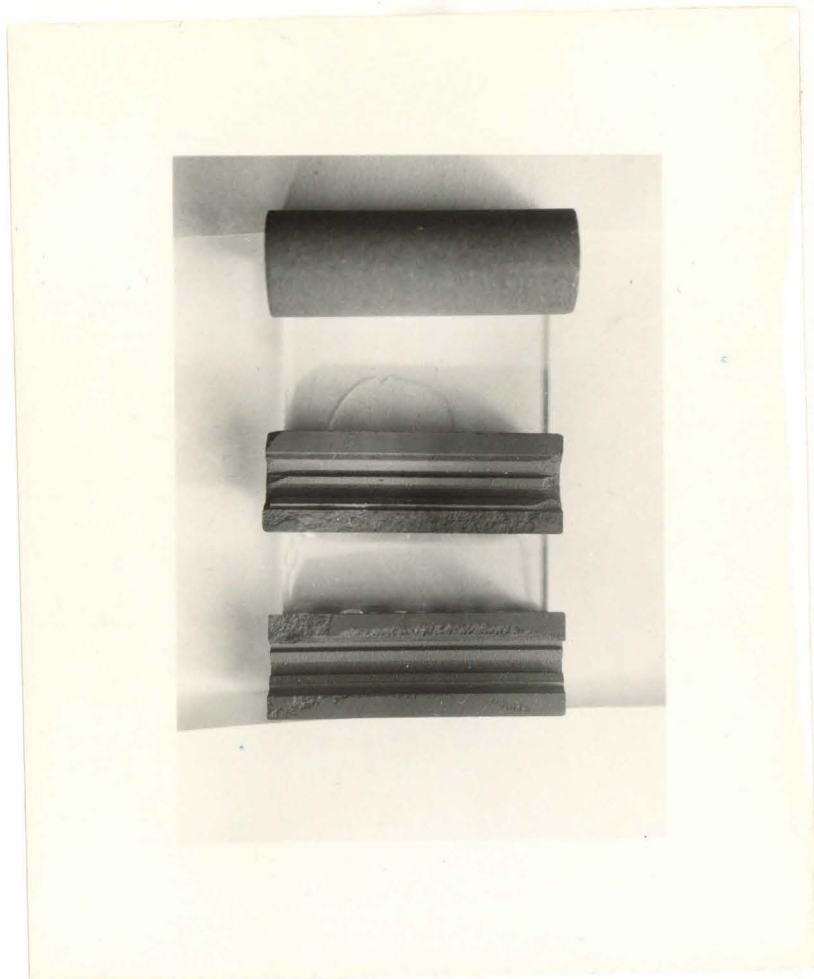


fig. 4. W3B carbon: untreated whole, (upper); cut in two (middle); with reduced silver (lower). 1.6 magnification.



fig. 5. Silver skeleton from ashing  
W3B impregnated carbon. 6.2 magnification.

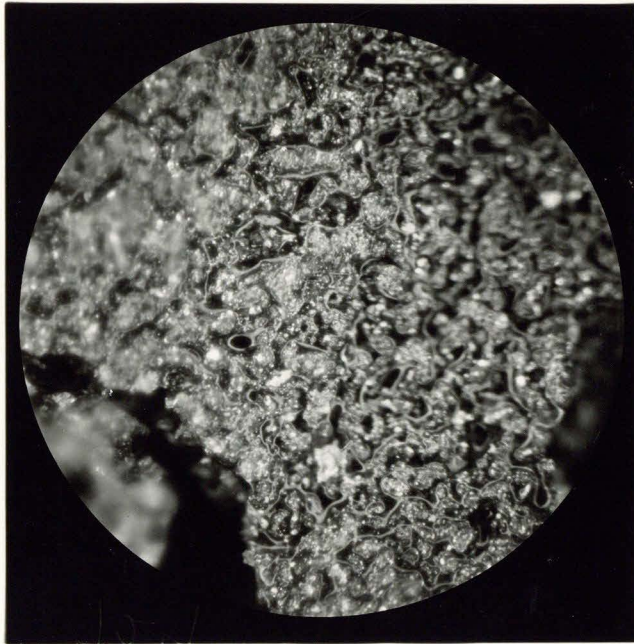


fig. 6. Surface of silver skeleton illuminated by reflected light and dark field. 70 magnification.



fig. 7. Material from broken silver skeleton illuminated by reflected light and dark field. 140 magnification.

#### A.4. Activation of the Carbon Silver Carrier.

Heat. It was found that the carbon silver carrier can be activated by heat when the method of silver oxide in ammonia is used to get the silver into the carrier, see Table V and fig. 9. With silver nitrate the solubility is so high that the amount of silver impregnated into the carbon makes such an activation unlikely since practically all the silver nitrate seems to come out again when the carrier is soaked in water without first reducing the silver (fig. 9). With relatively insoluble salts such as silver carbonate and sulfate the effect is not certain, though some data seem to indicate a maximum at about  $350^{\circ}$  just before the reducing action of the carbon starts at about  $400^{\circ}$ . The Katadyn beads seemed to be somewhat improved by heating. Efforts to activate the reduced carbon silver by prolonged heating in carbon dioxide atmosphere or by cooling from red heat in an oxygen atmosphere were unsuccessful. The maximum silver from the oxygen treatment was 3.5 gamma.

#### Electrolytic. 1. Charging Conditions.

By making the carbon carrier the anode in an electrically conducting solution and applying a potential more than the decomposition potential of water at about 1.7 volts (75) (or with carbon electrodes about 1.6 volts (74) (74a)) oxygen is usually evolved at the anode, and various sorts of oxidation processes take place (75).

To find out the best current density and time for this electrolytic treatment of the carbons a number of studies were made. Table VI shows the results with W3B using about .018 N. sulfuric acid as electrolyte, each point being the average of two carbons. The silver residue

TABLE VI

EMISSION WITH VARIOUS CURRENT AND TIME CONDITIONS								
Time	Current in ma. per carbon							
	2.5	5	10	20	40	80	160	400
4 min.								1.5 mg Ag
5				1.0	3.7	5.9		
10			1.5	5.0	10.0	9.8		
20	.76 (57.)	7.1	3.0? (44.5)	6.8 (34.2)	10. (30.6)	11.	9.8	9.6
40	1.3 (50.1)	3.? (44.3)	7. (36.1)	12.2	9.8 (18.7)	8.4		
80			9.7	7.8	6.8	5.3 (15.9)		
720					.3 (1.3)			

TABLE VII

SILVER IN CARRIERS AT VARIOUS STAGES OF PREPARATION AND USE						
Carbon	Ag Impregnated	Charge Loss	After Charging	Emission	Residue	
W3B	59.2 AgNO <sub>3</sub>	33.7	25.5	12.7	16.6	
W4B	123.5 AgNO <sub>3</sub>	49.6	75.7	12.1	53.3	
W4BC2	161.1 mfg. <sup>3</sup>	22.2	138.9	4.1	138.9	
W4BC3	242.6 "	45.5	197.1	5.9	197.7	
W4BC4	318.2 "	28.2	290.	14.3	287.9	

TABLE VIII

EMISSION, EMISSION WATER pH AND SALT SOLUBILITY OF ELECTROLYTES			
Electrolyte	Emission	pH of Water in 10 cc Emission Tube	Salt Solubility in 10 cc.
H <sub>2</sub> SO <sub>4</sub>	5.0 mg. Ag	2.7	39.4 mg.
HNO <sub>3</sub>	4.5	3.7-3.1	1420
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	3.8	4.7-3.4	slightly
K <sub>2</sub> HPO <sub>4</sub>	2.5	2.9	
H <sub>3</sub> BO <sub>3</sub>	1.4	3.8	
Na <sub>2</sub> CO <sub>3</sub>	.6	5.1	.25
HCl	.6	3.7	.01
NaOH	.6		.2



in the carbon after emission shown in parenthesis. Upon the basis of this table, the charging time and current was standardized at 50 ma. per carbon ( a current density of about 7 ma./cm.<sup>2</sup> for W5B), and a time of 50 minutes. The average potential applied across the electrodes of the cell for 6 carbons in the holder was 12 volts, and the total current .3 amp.

The charging was done in a two liter beaker. The cathode was a carbon rod and the holder for the carriers to be made anode is shown in fig. 8. The end plates and connecting piece are of bakelite and the two rods of carbon are covered with paraffin except for notches against which the carriers are held by a rubber band. The rubber band pulls the middle of the carrier toward the projection on the connecting piece, thus holding the carrier firmly against the notch in the carbon rod at each end, for contact. This arrangement was found to give a uniform activity to carbons charged together.

To attempt to increase the activity of the carriers, the carbons with reduced silver were charged with hydrogen as a cathode before being given the usual anodic treatment. Cathodic treatment might remove loosely adsorbed oxygen and leave space for more active electrolytic oxygen. This treatment did not affect the amount of silver emitted.

The electrolytic action takes place throughout the carbon (76) (71) (50) as shown by the following experiment. A W5B carbon 1" x 8 mm diameter was cut to a smaller size at various stages in the process by cutting the diameter to 5 mm in a lathe and cutting 1 mm from each end. Uncut, the silver given off was 4.5 mg.; cut to smaller size before silver nitrate impregnation, 2.0 mg.; cut after impregnation, 1.0 mg; cut after reduction, 1.1 mg.; and cut after charging, 2.7 mg. The surface of the uncut carbon was 7.5 cm<sup>2</sup> and its volume 1.25 cm.<sup>3</sup>,

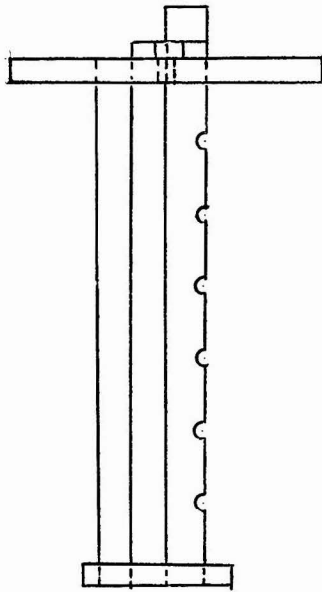
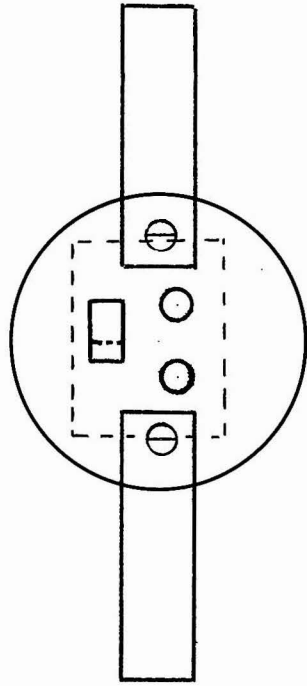


fig. 8 Anode Holder for Carbons

1/2" Size



the surface of the cut carbon was 4.0 cm<sup>2</sup>, the volume .45 cm<sup>3</sup>. The greater relative activity of the carbon cut after charging is probably due to cutting off an outer shell from which the silver has been electrolytically removed. This lead to an attempt to charge the carbons without the large electrolytic loss by using the property of the electrolytic action taking place, to some extent at least, throughout the carbon. A W3B carbon was charged by the insertion of a silver wire cathode along the axis of the hole in the center. Only .6 mg. was obtained from the silver emission.

In an effort to improve the amount of emittable silver compared to the silver left as residue after emission (Cf. Table VI), longer charging times were tried, with the following silver emitted: 50' (5.5mg.); 67' (2.4 mg.); 139' (1.9 mg.), and 247' (.5 mg.) With 67 minutes and longer (76) there was a light brown color in the emission tubes indicating oxidation products of the carbon had been formed (50) (45) (78) (51) (58) (74), though a brown color is not necessary for the existence of such products (45) (38) to be formed.

#### Silver in Carrier at Various Stages of Preparation and Use.

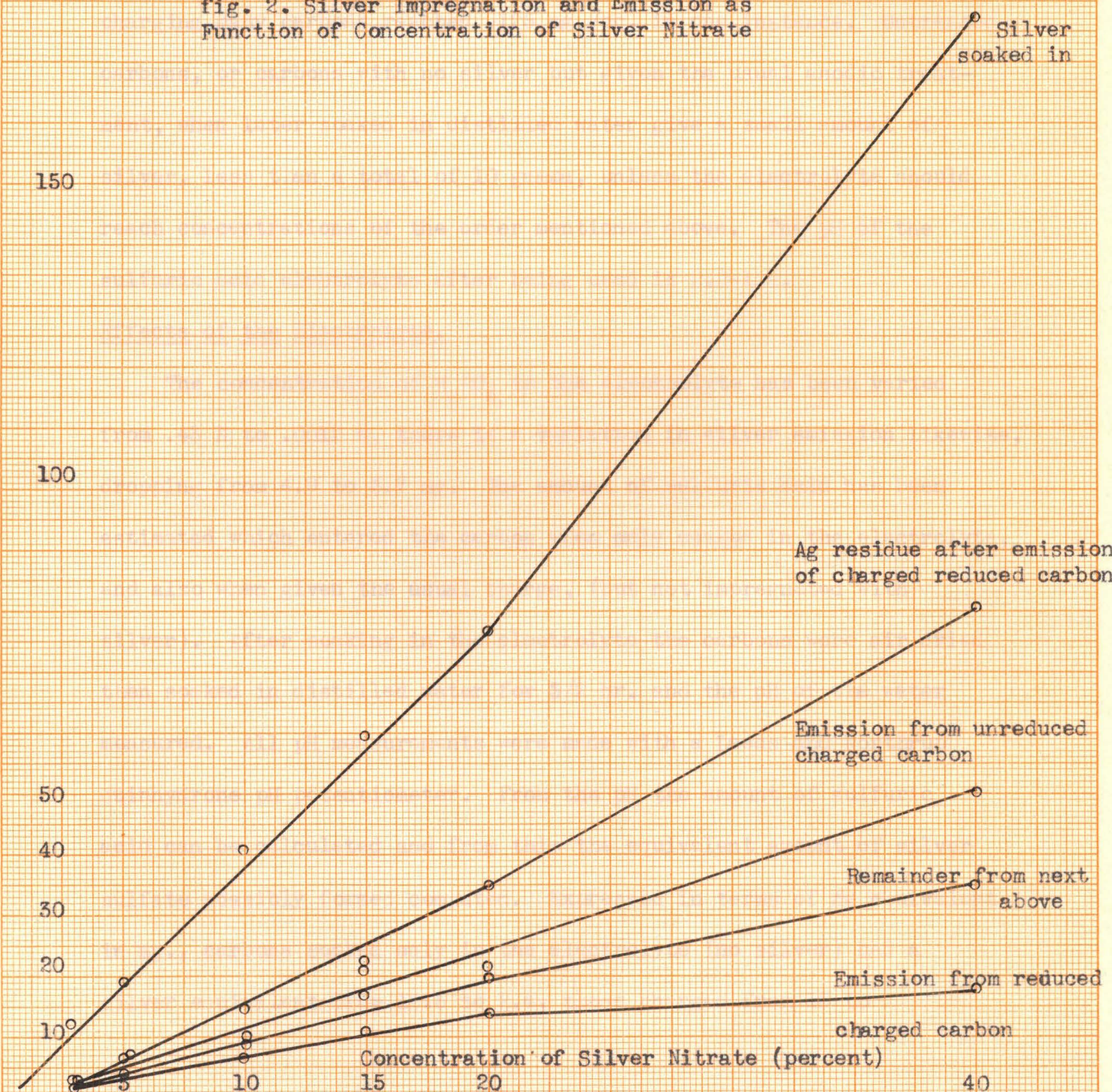
An idea of the fate of the silver impregnated into the carbon by silver nitrate or at the factory (8 carbons) shows the dependence on the process used. Table VIII and fig. 2 show the amount of silver originally in the carrier, the amount lost by charging, the amount remaining in the carbon after charging, the emission in 5/8 hour soak in distilled water, and the residue remaining after emission. The silver was determined by the usual ashing. Considerable variation in silver content of those factory prepared was noted.

With the charging of 52 carbons, no change of electrolyte, an average of 22 mg. of silver loss by charging was found by weighing the



2200 mg. Ag

fig. 2. Silver Impregnation and Emission as Function of Concentration of Silver Nitrate





silver obtained from filtering the electrolyte and washings from the cathode.

With a charge of 50 ma. for 30 min. 90 coulombs are used, of which  $1/3$  is used in the case of W3B (Table VII) to take silver from the carrier, and the balance has an oxygen liberating equivalent of 5 mg.  $O_2$ .

The silver concentration in the electrolyte (2 liters) after charging many carbons reached .125 mg./cc. in one instance. Untreated carbons, or carbons with no silver but given the usual anodic treatment, when later soaked in distilled water give a small amount of silver, less than a total of 10 gamma, unless the electrolyte should reach concentrations of the order mentioned above. The pH of the sulfuric acid electrolyte after being used is 1.0-1.9.

#### Effects of the Electrolyte.

The concentration of  $H_2SO_4$  in the electrolyte has been varied from .45 N to .0012 N, there is a variation in silver emission likewise, dropping from 4.9 to 3.7 mg. The amount of sulfuric acid has been estimated which entered the carbon when only soaked in the electrolyte, and also when given the usual charge, (but not impregnated with silver). After soaking in the electrolyte the carbons were air dried then soaked in distilled water for  $3/4$  hr. and the pH of the water measured. All pH measurements were made with a Leeds and Northrup quinhydrone pH potentiometer. From the pH the amount of sulfuric acid can be calculated and from this the equivalent amount of silver sulfate possibly formed computed. Expressed in terms of Ag e uivalent in mg., carbons soaked only in the electrolyte (no silver) had a silver equivalent from 12.5 to 2.4, those charged from 15 to

5 mg. over the above variation of  $H_2SO_4$  concentration. An unused unsoaked in electrolyte carbon reduced the pH to 2.5-2.4 (see below), or a silver equivalent of 5.8 mg. There is a marked increase of concentration of sulfate ions due to the charging. (76) (79) (80)

It is known that the various electrolytes produce different reactions at the anode in electrolytic processes (75). This is particularly true with carbon electrodes (38) (50) (74) (78) (51) (81) (45), and of course depends on whether the electrode takes part in the reaction (82).

The effect of the kind of electrolyte used in charging, on the activity, is shown in Table VIII giving various electrolytes, all in the range .01-.02 N. The ordinary figure for the solubility of the corresponding salt of the electrolyte anion (in 10 cc.) is also given. A greater emission (3.5 mg.) can be obtained from the chloride solutions (as with the sulfate) if a carrier with more impregnated silver is used. Other experiments have shown that the effect is independent of the cation of the electrolyte; barium, ammonium and sodium hydroxides were the same within experimental error, ferrous sulfate and sulfuric acid, sodium chloride and hydrochloric acid.

When the electrolyte is NaCl or HCl the carbon anode liberates chlorine (smellable) instead of oxygen because chlorine has a lower discharge potential than oxygen (92) (93). In time, however, oxygen and  $CO_2$  tend to be developed along with chlorine (94) (96) (102) (103), the proportion depending on the conditions (95) (77), and with oxygen chlorates are formed. The ordinary solubility of AgCl (97) or the formation of silver complexes (98) (99) (100) (104) seems to be inadequate to explain the high amounts of silver emission from carriers charged

in a chloride electrolyte, silver chlorate, however, is very soluble. The oxidizing action of chlorine has been used to prepare silver for oligodynamic purposes. (101)

The electrolyte used takes on the color of the corresponding silver salt of the anion, especially if the salt be relatively insoluble. The sulfate leaves a clear solution; chloride, a white cloud and white covering on the carbon; carbonate, brown in the top of the cell, while below; thiosulfate, dark brown crust on the carbons and some brown in solution; phosphate, brown above and lemon yellow below in bottom of the beaker; borate (hot saturated solution had to be used to get sufficient current), slight brown; hydroxides, brown; citrate, greenish brown; acetate, light brown.

Since the carbon itself can increase the hydrogen-ion concentration, distilled water can be used as a charging electrolyte. This property of carbon, to raise or lower the pH, is due to the formation of acidic or basic oxides and is determined by the temperature to which the carbon has been heated. (83) (84) (85) (64) (86) (87) (88) (90) (91) "If completely outgassed charcoal is treated with oxygen, the surface is covered with oxides, whose properties depend on the temperature and pressure of the treatment. These oxides will absorb from solution considerable quantities of acid, and sometimes also of alkali (i.e. they are sometimes amphoteric (89)). The actual proportions of acid and alkali absorbable depends on the temperature and pressure of the treatment with oxygen." (37) Those oxides formed in the 450° are acid in character. (83) (85)

This property of carbon in lowering the pH was utilized by making the water conducting (pH 3.8), with an unused carbon, in a copper

cylinder  $3/2$ " in diameter and 2" deep. A carbon so charged emitted only  $1/5$  that of a carbon similarly charged using sulfuric acid electrolyte. Difficulty was experienced in keeping the current density high enough, the resistance of the electrolyte increased rapidly when a current was passed through, at the end of charging was 6500 ohms. The concentration of silver in this small cell was 9  $\gamma$ /cc. after charging one carbon.

## B. Physico-Chemical Properties of Prepared Carrier.

### 1. Rate of Emission. 2. Stability of Emitted Silver in Solution.

The rate at which the silver is given out by the carrier is found by measuring the amount of silver in successive half-hour periods. When the log of the amount of silver emitted in a half hour is plotted against log of the time the relation seems to be a straight line, whether the silver comes from a charged carrier (fig. 1), or from just soaking the carbon in a silver salt solution (fig. 9), when almost as much silver comes out as was added in impregnation.

A property of water with the emitted silver is stability since the concentration after many days remains the same, and there is no visible precipitation. Another characteristic is that strong positive reactions are found when tested for the presence of the anion used in the charging electrolyte. Barium nitrate, for example, gives a precipitate with carbons charged in sulfate or carbonate electrolytes but not with nitrates. This may be expected since the dry carrier absorbs electrolytes, the concentration of which is further increased by the action in charging (p. 26). The amount of sulfate anion in the emission tube in the case of sulfuric acid was found to be about that necessary for the silver to be in the form of a sulfate. A test was made by determining the amount of emitted silver in the 10 cc. (by rhodanine), then making a solution of the same concentration of silver using silver sulfate. The two were tested for amount of sulfate using barium nitrate. The amount of precipitated material was about the same.

The sulfate solubility limit was not exceeded by soaking



six carbons (emission of 5 mg.) in succession in 5 cc. (final vol. 5 cc.)  
of distilled water, giving a total of 5 to 9.5 ug. per cc. depending upon

100 mg. Ag Emission

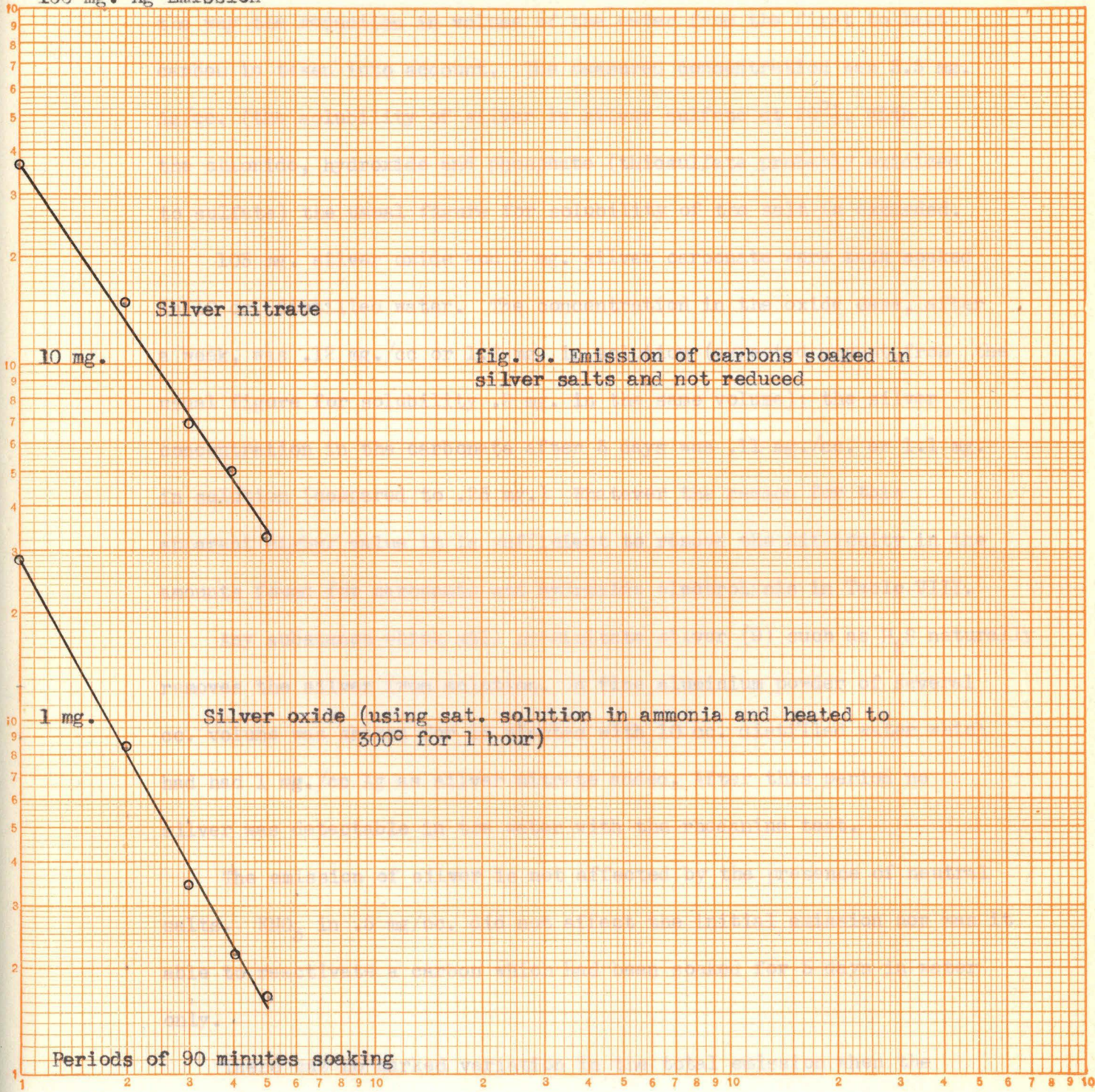


fig. 9. Emission of carbons soaked in silver salts and not reduced

volume of water varied from 10 cc. to 5 liters.



six carbons (emission of 8 mg.) in succession in 8 cc. (final vol. 5 cc.) of distilled water, giving a total of 6 to 9.6 mg. per cc. depending upon the way the reduction in volume of the water from the first to last carbon is taken into account. The measured concentration was 5.5 mg. Ag/cc. (the solubility of silver in silver sulfate at 20°). With the chloride, hydroxide and phosphate (thiosulfate probably oxidized to sulfate) the usual figure for solubility of the salt is exceeded.

103 mg. silver oxide and 3 mg. silver carbonate were each soaked in 10 cc. distilled water. The concentration in the oxide case, after a week, was .12 mg./cc or 1.2 mg. in solution (expected amount from the usual figure for solubility .2 mg. in the same volume); the silver concentration in the carbonate after 3 days was .11 mg./cc. or 1.1 mg. in solution (compared to .25 mg.) Whatever the reason for this apparent higher value it is sufficient to remove the difficulty in the amounts found for carbonate and hydroxide electrolysis in Table VIII.

Any substance which will precipitate silver (9) such as  $H_2S$  naturally removes the silver from solution. A fine aluminium powder of several cc. volume was shaken for 15 minutes with 10 cc. distilled water which had had 1 mg./cc Ag as silver nitrate added. After this period no silver was detectable in the water with the rhodanine test.

The emission of silver is not affected by the presence of neutral salts.  $KNO_3$  in .5 mg/cc. did not affect the initial emission nor was it able to reactivate a carbon which had been soaked for 5 days in water only.

There was no marked variation in the total emission when the volume of water varied from 10 cc. to 8 liters.

### 3. Stability and Destruction of Activity in the Prepared Carbon.

#### a. Time and Storage Conditions.

The activity of the carbon carriers is not affected by storage under ordinary conditions. Some carbons (a prototype with 75 percent lamblack) were prepared in 1939 by soaking in a 10 percent silver nitrate solution, reduced by just heating to red heat in a crucible, then charged with a current of 10 ma. for 15 mins. These carbons were wrapped in tissue paper and kept in a bottle which was taken to India and back by Dr. R. A. Millikan. Though there was a variation of almost 30 percent between individual carbons, the average emission was the same a year later, .75-.8 mg. in  $3/4$  hr., as when made in 1939. The relation between the amount of silver and charging conditions was such that a recharge (without emission) at 10 ma. for 10 mins., or 50 ma. for 37 mins. all gave the same amounts of silver, within an average of 5 percent, as the carbons which had been given no further treatment after storing.

Another set of standard carbons were stored for periods up to 9 months under the following varied conditions; wrapped in cellophane, sealed in a glass tube above solid sodium hydroxide (to remove water), in a glass sealed tube with calcium chloride in a  $10^{-2}$  mm Hg pressure vacuum, and in a sealed glass tube above about 1 cc. of saturated  $H_2S$  water. These carbons when made had an emission of 4.5 to 5.0 mg. Ag in  $3/2$  hrs. After 9 months in wrapped cellophane and dry air stored carbons were unaffected, those in vacuum slightly less active, about 3.7 mg. Ag, and those with  $H_2S$  gave, in one instance, .1 mg. and .0025 mg. in another, the  $H_2S$  carbon tested at two months gave .8 mg. The  $H_2S$  carbons unfortunately were all wetted by the water. No smell of

$H_2S$  was present when the tubes were opened; apparently there had been sufficient silver to remove the sulfide and still have some active silver left.

#### Chemical.

In addition to the  $H_2S$  poisoning just mentioned, the carriers can also be poisoned by soaking in a 1 percent NaCl solution, broth or pentone, for example. The poisoning was very marked after 1 min. exposure and 10 or 30 mins. nearly destroyed it. These poisoned carriers can be reactivated by recharging, although this is not as effective as the original unpoisoned carrier. The amount the reactivation can produce is indicated by the results of long charging (Table VII and p. 25). Carbons charged at 10 ma. for 10 mins. giving about 2.5 mg., when recharged the same amount gave 2.25 mg., but when re-treated with silver nitrate, etc., gave about 3.0 mg. This type of result holds for short, low charging conditions, with the standard charge it is different. Carbons giving 9.1 mg. average when recharged gave an average of 1.5 mg. additional; if retreated after emission, they gave an average of .8 mg. Ag more than did the first time. The ash from the only recharged was 2.2 mg., while from the retreated and soaked was 55.8 mg., and retreated but not resoaked, 37 mg.

#### Cathodic Reduction.

The activity may be destroyed by charging the standard carbon cathodically, as shown by the following typical figures (50 ma.); no reduction, 4.6 mg.; 3 mins. 3.75; 25 mins., 5 mg. Ag.

#### Heating.

The destruction of activity by heat is shown in fig. 10 where sulfuric acid and sodium carbonate electrolytes are shown. This may be

compared to fig. 3, the difference being in the intimacy of contact between the silver and carbon. Carbon carriers soaked in silver salts and heated show this same destruction of activity (reduction) above  $400^{\circ}$ .

The electrode potentials of the variously treated or untreated carbons were measured with respect to each other and metallic silver by Pogendorff's compensation method (105). While accurate electrode potential values are not to be expected without considerable effort in rigidly controlled conditions, yet the figures given are probably well within the correct order of magnitude, in volts, shown in fig. 11.

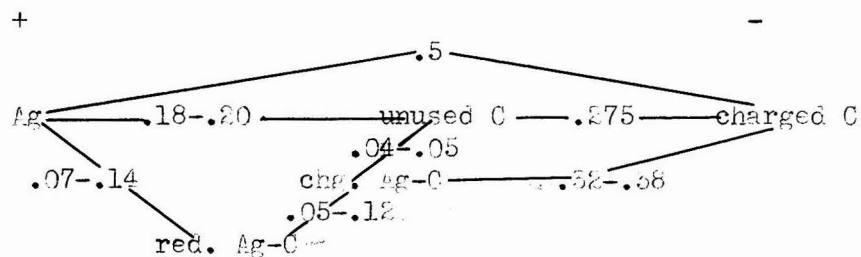


fig. 11

#### Electrode Potentials of Carriers



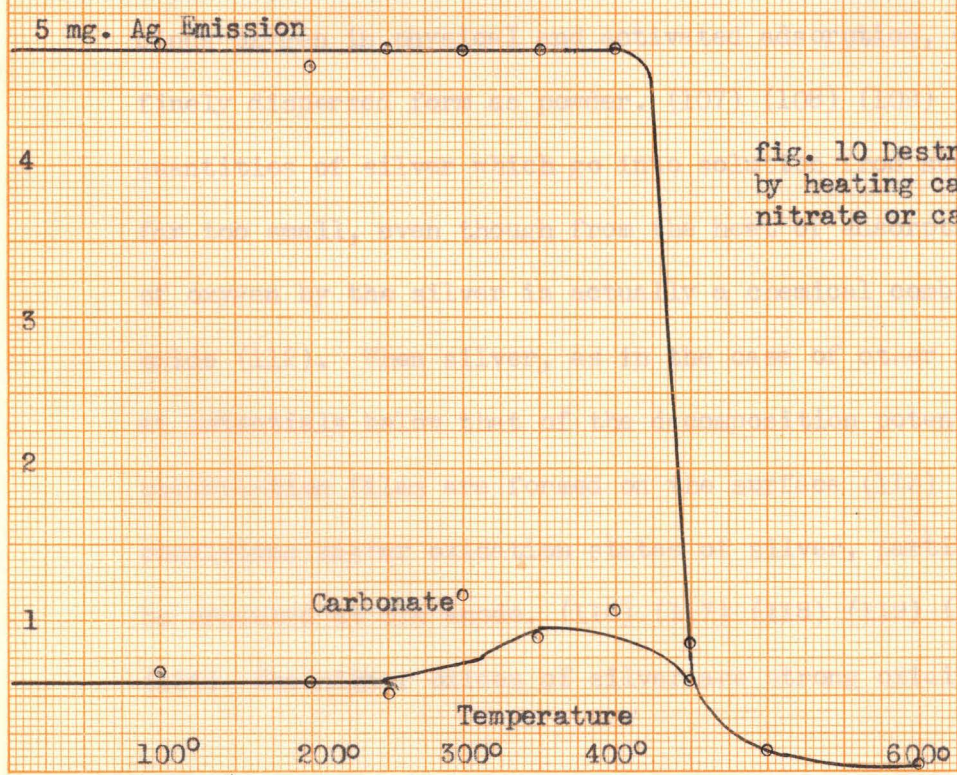


fig. 10 Destruction of activity by heating carbons charged in nitrate or carbonate electrolyte.



## V THEORETICAL DISCUSSION

In order for silver, in its reduced state, to go into solution, an oxidation, i.e., the removal of electrons of the metal, must take place. Electrolytically this may be described in the following terms (106): "At the anode, where electrons pass from the solution to the wire, some substance is oxidized. This oxidation may be the liberation of oxygen gas, the liberation of halogen gas, the dissolving of a metal electrode, the deposition of a higher oxide such as  $PbO_2$  or  $MnO_2$  upon the anode, or the oxidation of some substance present in the electrolyzed solution such as a ferrous salt.

The carbon silver carrier when made the anode is a surface exposing both silver and carbon to the electrolyte. Carbon does not form an ion and go into solution (45), but silver does.

Gas, oxygen or chlorine, also may be evolved and adsorbed. In the conditions in standard preparation large amounts of oxygen are adsorbed.

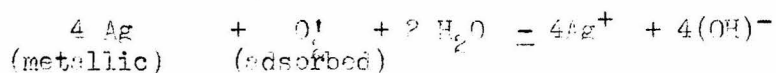
The relation of silver to oxygen may be briefly considered. Silver binds oxygen in physical and activated adsorption, especially in a finely dispersed form as powder. (107) (108) (109) (110) (111) The quantities of silver which go into solution from such an activation are far too small, even though from the heat of adsorption the adsorption of oxygen by the silver is actually a chemical combination as silver oxide (112). When silver, as in the case of other metals, is made anode at potentials below that of the decomposition potential of water, oxide polarization films are formed on the surface (113) (114). Under certain conditions higher oxidation states of silver, particularly oxides, may be produced at the anode. (116) (117) (118) (119) (120) (121) (122) (123) (124) The higher oxides of silver are strong oxidizing agents (125)



and decompose under the influence of water. These salts are not obtained in pure form, but have the silver salt of the electrolyte included in varying quantities (55). These higher oxides may be the source of the active silver.

Silver carbonate deposit is formed on the electrode (Ag) when using a carbonate electrolyte (115). The existence of suboxides of silver from  $Ag_4O^+$  to  $Ag_2O^+$  have been reported, but there is considerable doubt concerning not only the existence but especially the stability in solution. Isolation of them has not been accomplished. (55) (114) (124)

Oxygen gas itself has not an appreciable activating effect on the carrier (p. 22). From the energy considerations it is to be expected that the oxygen should prefer the carbon to the silver since the free energy of  $Ag_2O$  is -2590 cal./mol. and that of CO -33010, and  $CO_2$  -94450, (125), and the heat of adsorption of oxygen on carbon varies, depending on the kind of adsorption, up to 64,000 cal./mol. (126), say 50,000 cal./mol. (86) (128) Oxygen adsorbed at room temperatures can only be removed from the surface in combination with the carbon (127). This means that the ordinary adsorbed oxygen on the carbon will not have the energy to send silver into solution, in fact, to make the following reaction proceed:



27,000 cal./mol. (neglecting the large amount necessary in energy to desorb the oxygen) would be needed, this is equivalent to 0.5 volt. Thus to make a local element function in order to send silver into water, a greater potential would be needed than indicated in fig. 11.

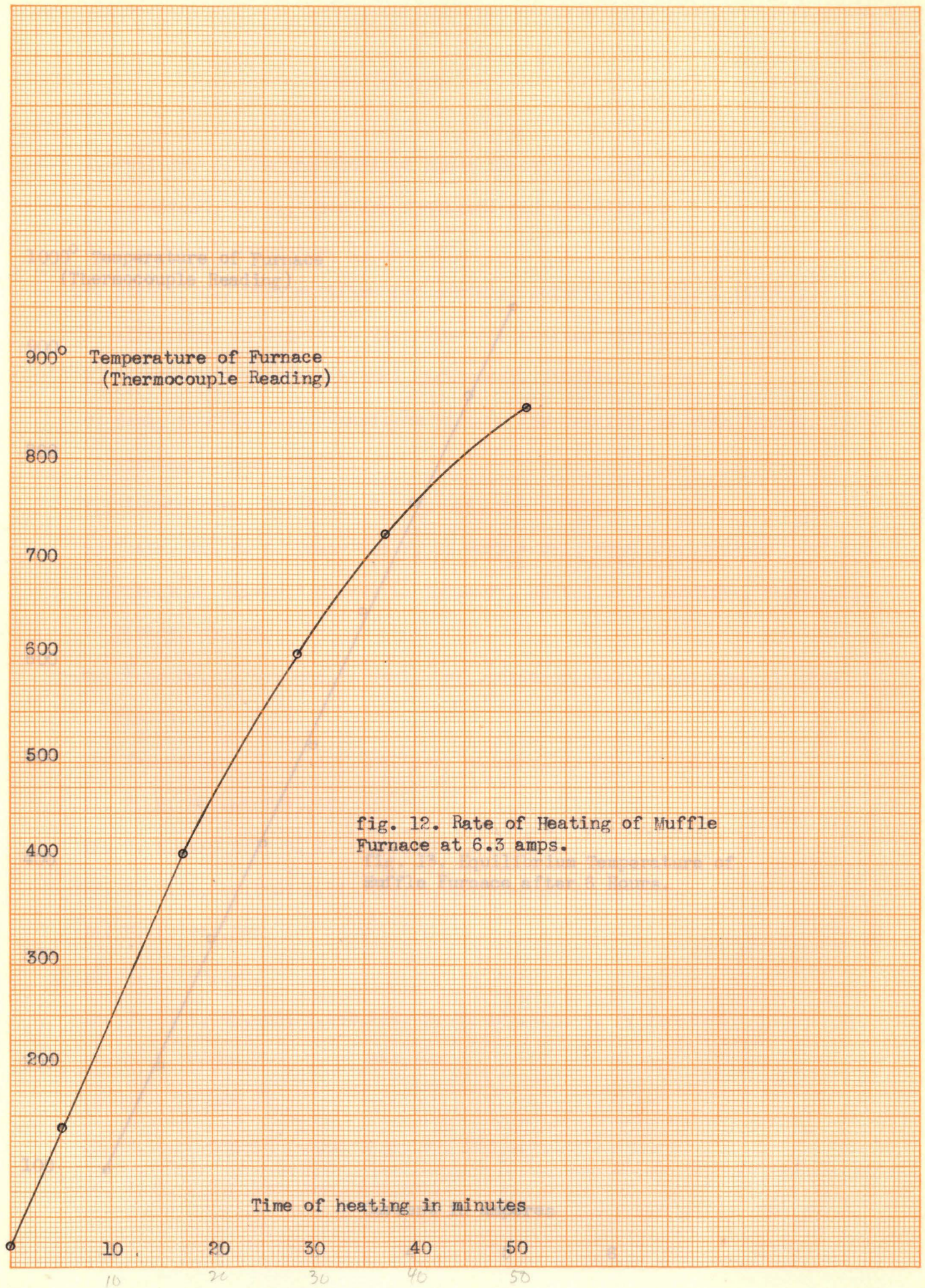
The oxidation power of carbon is generally ascribed to the chemisorbed layer of oxygen on its surface (83) (129). The catalytic activity is determined by the structural type of the carbon (130), and is an optimum for the acidic type of surface (85), this fits with the superiority of lamoblack carbons of the type used. The effect of different electrolytes may be partly explained by the formation of obstructing films (131). Though carbon forms many types of bonds with oxygen (128) (37) (41) (64) (132) (86) (55) (56) (132) (133), there is one type of particular interest. There is a primary oxide of black carbon formed by electrolytic oxidation (38) (56) (132) which is a strong oxidizing agent and whose formation varies with the electrolyte used.

While the character of the emitted silver is not yet certain, it is not probable that it is emitted in the form of a hydroxide, since this, in a saturated solution, has a pH 8.4 (134), and the emitted silver solutions are always acid, irrespective of the electrolyte used.

## VI CONCLUSION

A process has been developed, in which a carbon carrier composed mostly of lampblack is used, to obtain a source of silver for oligodynamic action. The process consists of: impregnating the carbon with silver nitrate solution and reducing the silver to a finely dispersed form in the carbon by heating, and charging electrolytically as anode. Through this oxidation process whose mechanism is not yet understood, the carbon silver carrier is activated so that it will emit silver when the carrier is soaked in water. The prepared carrier is unaffected by heat up to 500° C. and it retains its activity over periods of more than a year.







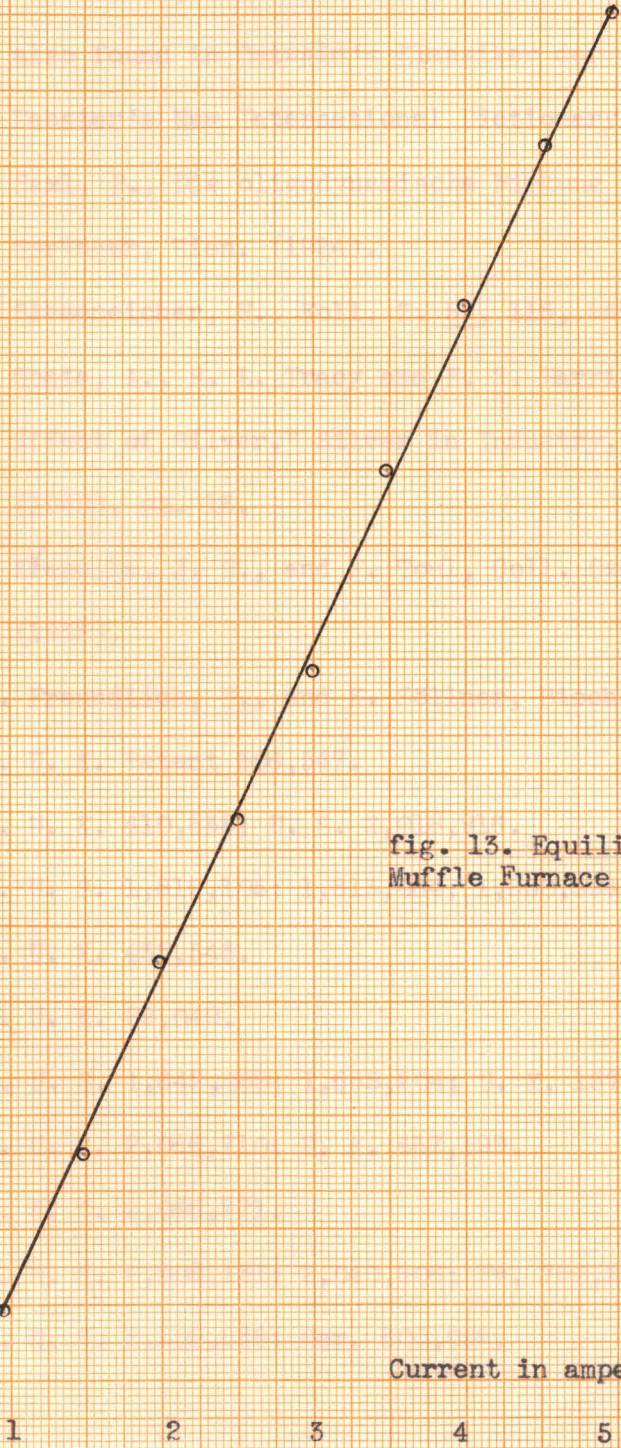
1000° Temperature of Furnace  
(Thermocouple Reading)

900  
800  
700  
600  
500  
400  
300  
200  
100

1 2 3 4 5 6

Current in amperes

fig. 13. Equilibrium Temperature of  
Muffle Furnace after 6 Hours.





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