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THE BROMINE AND BROM ETHOXY COMPOUNDS
OF PHENANTHRENE.

A Thesis submitted to the faculty of the Graduate
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INTRODUCTION.

The well known hydrocarbon phenanthrene was first discovered and investigated in 1872 by Fittig and Ostermayer, who separated it from the higher boiling distillation products of coal tar. These men further proposed in their original paper, by reason of its oxidation to o diphenic acid and the analysis of its quinone and other derivatives, the constitutional formula attributed to it at the present time.

Since the day of these early investigators, many workers have attacked its numerous compounds and substitution products. Great fascination was lent to the research by the early discovered fact that it was the basal substance of the morphine alkaloids. At the present time active investigation is still being carried on in this direction, with the result that one or more closely related compounds have recently been prepared, and the synthesis of morphine itself grows daily nearer.

It was hoped to find also, among the derivatives

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of phenanthraquinone, various dyes similar to the anthraquinone series. This desire has not been realized as yet, although the field is by no means exhausted.

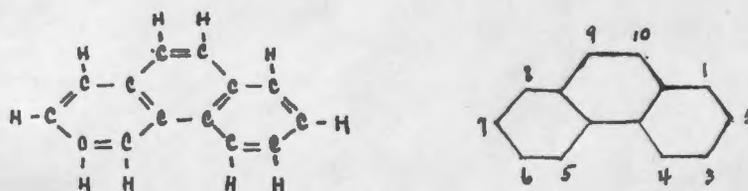
In connection with the former line of research, there may be mentioned, among several others, the extensive work of Professors Robert Pschorr of the University of Berlin, and Julius Schmidt, of the Königlich-Technischen Hochschule at Stuttgart, and their students.

Apart from its relation to various alkaloids, the especial claim of this hydrocarbon to importance is in a large measure due to its comparatively cheap and plentiful source of supply. It occurs to a considerable percent in the coal tar distillates, in which it was originally discovered, notably in that fraction which passes over between 270 and 350°C., and is commonly called anthracene oil, from its most important constituent. In commercial practice, crude anthracene is largely recovered from this fraction, for the manufacture of the valuable dye alizarine. The process consists in cooling and fil -

tration of the semi-solid oil, and subsequent treatment of the solid residue to heavy pressure in the hydraulic press, after which the cakes are broken and washed with coal tar naphtha or other light oils. This last washing removes the associated phenanthrene in a more or less pure condition, and the latter is thus produced as a by-product almost worthless at the present time. As stated in epitaph by the text-books, the residue of phenanthrene is usually burned for the production of lampblack, after recovery of the light oils by a process of distillation.

Constitution of Phenanthrene.

In constitution phenanthrene has the empirical formula $C_{14}H_{10}$ and a structural formula as follows.

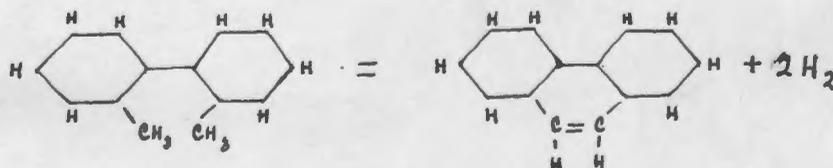


The various substitution points are commonly

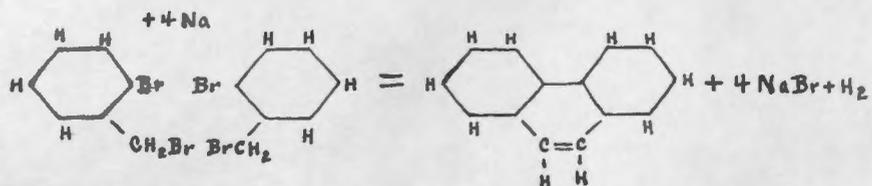
numbered as shown. The double bond and two carbon atoms at 9 and 10 form the weakest place in the ring and are frequently called the "bridge." It is at these two positions that the compound oxidizes to form its quinone, and substitution in general takes place easiest there.

The constitution has been established by several reactions, three of which are as follows.

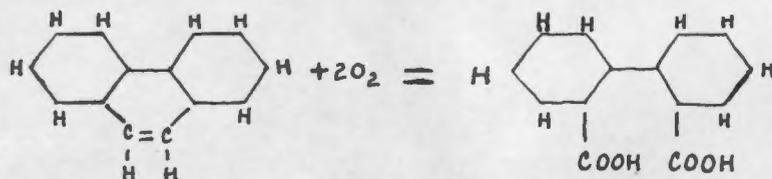
1st. By its formation from toluene, dibenzyl, stilbene, and especially *o*-ditolyl, on leading their vapors through a red hot tube.



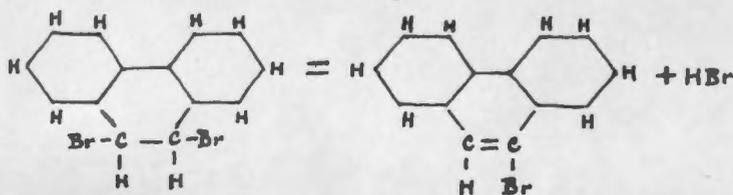
2nd. By its formation, with anthracene, from *o*-brom benzyl bromide on treatment with sodium and subsequent oxidation.



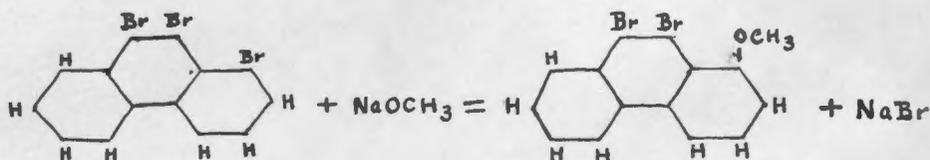
3rd. By its oxidation to o diphenic acid



Pertinent to this particular research also is the easy formation of the dibromide addition product and its rapid decomposition at 100°, to the 10 monobromphenanthrene.



The reaction also between sodium alcoholates and bromine substitution products will be clearer if stated as follows.



To make more apparent the causes of the difficulties experienced in working with higher phenanthrene compounds, the author has made out a list of the theoretically possible substitution products. In unmixed substitution products, the theory gives 5 mono, 25 di, 60 tri, and 109 tetra. Above the penta will be seen that the number again diminishes. With mixed derivatives the possibilities become almost immeasurably numerous.

Object of the Research.

The original purpose of this investigation was to prepare and study more thoroughly certain ethoxy and methoxy dibrom phenanthrenes previously discovered by Miss Edith M. Thomas. These had been produced by treating mixtures of the lower bromine compounds of phenanthrene with sodium methylate and ethylate respectively, and were described by her in a thesis presented in 1903 for the Master's degree at the University of Minnesota.

After working in this direction with indifferent success, it was later decided to prepare a number of the higher brom phenanthrenes, with the intention of finally substituting ethoxy or other groups for the bromine in these. Small quantities of three or four higher bromides were produced, including a new tetrabromide, but the treatment of these later compounds to replace the bromine was not carried out as planned. The research was begun at the suggestion of Dr. Geo. B. Frankforter and carried forward under his direction.

Outline and Discussion of the Work.

For the production of the red ethoxy and methoxy compounds, six preparations of 9-10 dibromide and 10 brom phenanthrene were made at non-consecutive times. Four of these were ultimately treated with sodium ethylate and one with sodium methylate. The sixth preparation was treated with additional bromine to form a higher substitution product. The sodium ethylates were successful in producing a red compound in each case, but sodium methylate had no definite effect.

Following the above work, five different experiments were next carried through to produce higher brom compounds directly. In the first of these the bromination was made in carbon disulphide solution and in the second vapors of bromine were passed over the boiling hydrocarbon. In the last three, solid phenanthrene was treated with liquid bromine undiluted. C.P. Phenanthrene was used throughout the experiments.

In discussion of the preparations of the dibromide

and monobrom compounds there is little to be said. They were made according to the methods of Miss Thomas and later of Hayduck (see List of Papers, p.20). These compounds are not the proper starting point for the production of an ethoxy dibrom phenanthrene. But it was thought best to use, for a time, the method by which the latter had been first prepared. To produce such an ethoxy dibrom compound, it is evident from the reaction (p.6) that a tribrom phenanthrene must originally be present. If the red substance prepared in this investigation is composed entirely of the former, it has then resulted only from the presence of the tri compound in the monobrom mixtures. The four experiments performed gave very small yields of red substance, and the reason is thus plainly apparent. In this case it is seen that the purer the raw materials used the poorer is the gain in the product sought.

Concerning these ethoxy experiments it must also be mentioned that the red compound produced, while very probably original with Miss Thomas and previously unknown,

has not been identified with certainty, by the author, as ethoxy dibrom phenanthrene. In the table given on page 16, it appears similar, except for the melting point, to the later discovered 2-7 Dibrom phenanthrene quinone, prepared by Schmidt and Junghaus, and has a similar percentage of bromine. (See table p. 14). Further, methoxy and ethoxy compounds and their bromine derivatives will be seen to be generally colorless, where color is mentioned, while quinone and hydroxy compounds are uniformly colored. Even Miss Thomas' methoxy compound is colorless, which should be noted. It appears possible, therefore, in view of the deep red shade of the substance, that in some manner the brom ethoxy compound first produced may have become oxidized to a quinone, or a hydroxyl group have been introduced by saponification. This is made the more likely by the fact that in some cases the color was developed very slowly.

Whether the reaction is due, however, to the introduction of an ethoxy or a hydroxyl group or to the formation of a quinone, it seems probable, in either case, from

the analyses (36.6 - 38.4% Br - see table p. 14,), that the compound produced is a mixture of mono and dibrom derivatives of similar properties. The ethoxy and hydroxy dibrom phenanthrenes and the dibrom quinone, all have percentages above 42%, and the similar monobrom derivatives all under 31%. The introduction also, of more than one ethoxy or hydroxyl group is unlikely in view of its necessitating a tetrabrom compound, and an ethoxy or hydroxy quinone will be seen not to lower the bromine percentage to that of the compound analyzed. In conclusion then, it had best be said that the composition of this red substance remains still decidedly in doubt, and demands further experimental work for its final solution.

The most important fact to be mentioned concerning the second half of the investigation, is the preparation of a new tetrabrom compound. The other preparations were small in amount, and are of corroboratory interest only, since they appear identical with compounds made by previous investigators. They were originally to be used in the production of various other derivatives; but this design

was not carried out according to the intention. In every case, in these experiments the investigation was much impeded by the production of large quantities of sticky oils, that contained recoverable crystalline solids only in small proportion, and in some cases not at all. The oils were undoubtedly mixtures of various liquid and solid bromine compounds and their isomers. A number of addition products were also possibly present, since on distillation much of H Br passed off in some cases, with little sign of decomposition. The more unimportant compounds prepared, are as follows:

- 1st. A dibrom compound, crystallizing in yellow tables and melting at 158° ; similar to that produced by Zetter, which melts at the same temperature.
- 2nd. A dibrom melting at 208° , and possibly the same as the one melting at 202° prepared by Hayduck and Limprecht.
- 3rd. A tetrabrom of long silky yellowish needles, melting at 187° and very probably the tetrabrom of Zetter, melting at 185° .

The new tetra bromide produced melts at 235° and crystallizes in long silky fibres that matt easily together on a suction plate. No mention of this compound has been found during an extensive search through the phenanthrene literature. The impure mixture, from which it was isolated, appears, from its melting point of $180-225^{\circ}$ and other properties, to be possibly largely composed of the tetrabrom phenanthrene, prepared by Zetter and melting at $183-185^{\circ}$.

The following tables give a list of the various bromine compounds of phenanthrene and some of their properties and bromine percentages. It should be noticed that the white methoxy dibrom compound made by Miss Thomas appears identical with that produced by Pschorr and Jaeckel, whose results were published in 1900. (See table p. 19).

Table 1.

Bromine Percentages.

Analysis of red compound.

1st.	38.40
2nd.	37.56
3rd - Light colored	36.60
Miss Thomas'	43.64

Calculated for

$C_{14}H_8Br_2$	47.4
$C_{14}H_7Br_2OH$	45.5
$C_{14}H_6Br_2O_2$	43.7
$C_{14}H_7Br_2OC_2H_5$	42.1
$C_{14}H_5Br_2O_2OC_2H_5$	39.0
$C_{14}H_6Br_2(OC_2H_5)_2$	37.7
$C_{14}H_9Br$	31.1
$C_{14}H_8Br OH$	29.3
$C_{14}H_7Br O_2$	28.9
$C_{14}H_8Br OC_2H_5$	26.5

Table 2.

Bromine Compounds.

Dibromide. ($C_{14}H_{10}Br_2$).	Melts	
Four-sided prisms.	98°	Hayduck, Zetter Fettig & Ostermayer
Monobrom (10 $C_{14}H_9Br$)		
Yellow needles	63°	Hayduck, Zetter
Thin white prism.	63°	Limprecht.
Dibroms.		
2-7, Long, colorless needles.	199-200°	Schmidt
??, yellow. white, cryst. powd.	202°	Hayduck, Limprecht.
?-10, white needles	112-113°	Werner
??, Long white needles	148°	Zetter
??, Tables.	158°	Zetter
Tribroms.		
???, White, silky needles.	126°	Zetter, Hayduck Limprecht.
Tetrabroms.		
???? White to pale yellow	185°	Zetter.

	Melts.	
Hexabrom		
Snow white needles.	245°	Zetter
 Brom Quinanes		
2, yellow tables and needles	233-234°	
?, Nodular aggregates	126°	
 Dibrom Quinones		
2-7, Fiery brick red	323°	
??. Yellow warty masses	230°	

Table 3.

Hydroxy, Methoxy and Ethoxy Phenanthrenes.

	Color	Crystallization	Melting Points.
Hydroxy.			
2	White	Lustrous leaflets	168°, 169°
3	Colorless	Group ^s of needles	118-119°, 122-123°.
10	White (Oxidizes pink)	Lustrous needles	148-149°, 152°
Methoxy.			
1	White	Long silky needles	103°, 105-106°
2	White	Leaflets	99°, 100-101°
3	White	Lustrous plates	63°, 60-61°
4	White	Glistening Plates	68°
Ethoxy.			
3	White	Crystals	42°
Dimethoxy.			
2-3	White	Plates	131°
3-4	Colorless	Lustrous plates	44°
Trinethoxy.			
1-5-6	Colorless	Leaflets	135°, 138°

Table 4.

Hydroxy, Methoxy and Ethoxy
Phenanthrene Quinone.

	Color	Crystal Form	Melting Points.
Hydroxy quinones.			
2	Violet black	Slender needles	280-283°
3	Brick red	Needles	No M.P. Sublimes.
3	Yellow red	Needles	330°
4	Red	Powder	285°
Methoxy quinones.			
2	Dark red	Needles	170-171°
3	Orange	Needles	208°, 204-205°
Ethoxy quinones.			
2	Red	Leaflets	160-161°
3	Orange	Needles	207-208°
Dimethoxy quinones.			
2-3	Dark red	Needles	304°

Table 5.

Methoxy Brom Phenanthrenes.

and Brom Quinones.

	Color	Crystal Form	Melting Points.
Methoxy			
2 Meth. ? Brom		Needles	176°
3 Meth. ?? Dibrom	Pale red	Needles	150°
4 Meth. ?? Dibrom	Colorless	Needles (Miss Thomas)	152° 152°)
Dimethoxy			
2-3 DiM ?? Dibrom		Needles	160°
3-4 DiM ?? Dibrom		Needles	124°-125°
Trimethoxy			
1-5-6 TriM. ?? Dibrom	Colorless	Needles	139-141°
2 Methoxy			
?? Dibrom Quinone	Reddish yellow	Needles	160°
2-3 Dimethoxy			
? Brom Quinone	Brownish "	Crystals	158°

(No Hydroxy or Ethoxy Bromides or Brom Quinones
were found).

EXPERIMENTAL PART.

Preparation of the 9-10 Dibromide and 10
Brom-Phenanthrene.

Preparation 1.

Ten grams of phenanthrene were dissolved in 30 c.c. of carbon tetrachloride in a small flask, and the vessel placed in ice. When the liquid had reached the temperature of the ice, it was found that this amount of solvent was insufficient to keep the hydrocarbon in solution, and 10 c.c. more solvent were therefore added. Into this, then, 5 c.c. of bromine (about two molecules), dissolved in 5 c.c. tetrachloride, were slowly poured, the reaction liberating copious fumes of hydrobromic acid. There occurred a slow formation of medium sized crystals, which finally filled up the liquid to form a fairly solid mass. When the evolution of gas had become very slow, more solvent was added and the flask allowed to stand 3 hours. At the end of this time the crystals were drained, washed by decantation with tetrachloride, and recrystallized from hot chloroform. $5\frac{1}{2}$ grams were obtained of

light yellow tables, melting at 91° . The pure $C_{14}H_{10}Br_2$ melts at 98° .

On dissolving on the water bath for further purification, the preparation was accidentally allowed to go to dryness and by this process the dibromide was partially decomposed. The mass was therefore heated until no further HBr fumes passed off, a characteristic odor being noticed at the same time, which was not due to HBr. In the dish a dark-red viscous liquid remained, which would not crystallize from alcohol or ether. It was found to be very soluble in ether, but only moderately in chloroform, and much less in alcohol.

Preparation 2.

Ten c.c. (or about 6 molecules) of bromine, dissolved in carbon disulphide, were slowly added to 10 grms. of phenanthrene in 50 c.c. of CS_2 , with the vessel packed in ice as in the previous preparation. The reaction proceeded in a similar manner with the evolution of HBr. The crystals produced were dislodged, washed into a crystallizing dish, and allowed to stand over night, at the

end of which time both the solvent and the excess of bromine had evaporated, and the preparation was recrystallized three times from chloroform. Seven grams of pure crystals were obtained, which were similar to the preceding ones, but melted at 100°. In the mother liquor from the crystallizations, a few star-shaped clusters of thin yellow needles were noticed; but these were not enough to warrant further investigation.

Preparation 3.

Thirty grams of phenanthrene dissolved in 100 c.c. of carbon disulphide were treated, as in Preparation 2, with 15 c.c. (or about 3 molecules) of bromine, allowed to stand for a few hours, and poured into a crystallizing dish. On the following morning the mass still contained carbon disulphide and bromine. The preparation was then left untouched for several days, and the dibromide having partially decomposed during that time, it was heated on the water bath until HBr fumes ceased to come off. A very strong odor was noticed, different from Preparation 1. Yield of oil, 25 grams.

Preparation 4.

Twenty grams of phenanthrene, dissolved in 100 c.c. of carbon disulphide were treated with 10 c.c. of bromine. The flask in this preparation was strongly cooled and the HBr fumes scanty. After standing two hours, the solvent was decanted from the yellow crystals and the latter placed in the sun until free from bromine. Yield 10 grms., melting at 104° . A small amount was continuously heated and kept liquid until HBr fumes ceased. The solidified $C_{14}H_9Br$ melted at 57° .

The solvent, decanted from the original crystals, gave on spontaneous evaporation 17 grams of a light yellow semi-oily mass, similar in appearance and odor to the preceding oils. It was heated at 100° for a short time, very little HBr being given off. Strong cooling did not cause it to solidify.

Preparation 5.

Fifteen grams of phenanthrene were dissolved in carbon disulphide and treated, as in the preceding experiments, with 18 grams of bromine. There was obtained from

this 2.5 grams of yellow crystals of dibromide, which were heated on the water bath until HBr fumes ceased. The solidified compound gave a melting point of 60°. The yellow ill-smelling oily mass left from evaporation of the carbon disulphide was treated with ether, in which the larger portion dissolved with great ease, leaving however about a gram of a light yellow powder, melting at 208°. This possibly contained a quantity of the dibrom compound mentioned by Hayduck and Limprecht, which melts at 202°.

From the evaporation of the ether 18 grams of a dark-brown oil were obtained. This on distillation gave off a small amount of water with violent bumping, and later great quantities of HBr fumes. The distilling flask cracked at this point and the operation was discontinued, but in a later attempt the oil passed over between 335 and 350°, liberating large quantities of HBr. The distillate appeared similar to 10 C₁₄H₉Br.

Preparation 6.

Twenty grams of phenanthrene, dissolved in 70 c.c. of CS₂, were treated with two molecules of bromine. The

flask was cooled with a mixture of ice and salt, and the bromine added very slowly from a separatory funnel, very little HBr being liberated. On partial evaporation, a heavy precipitate of the dibromide was deposited, and from this the solvent was decanted, and the crystals washed and treated to form the 10 monobromide. This latter on recrystallization with carbon disulphide yielded $18\frac{1}{2}$ grams.

Six grams of oil were left after evaporation of the solvent and bromine. On distillation great quantities of HBr were given off, as in the preceding preparation, and the oil passed over between 335 and 355° . The distillate solidified in the receiver to a yellow brown mass having the consistency of cheese. The crystallization showed it to be 10 $C_{14}H_9Br$. Melting point 63° .

Treatment of the Bromine Compounds with
Sodium Ethylate.

Experiment 1.

The 5 grams of oil resulting from the 1st Preparation of the 9-10 Dibromide, consisted mainly of 10 monobrom phenanthrene with small amounts of isomers and higher bromides. This was dissolved in a small quantity of absolute ether, poured into 60 c.c. absolute alcohol and a number of short pieces of sodium wire slowly added, the reaction between the sodium and the alcohol being very violent. After a few moments dark red crystals began to collect at the bottom of the flask. This continued for a short time; but later the oil appeared to be deposited and more ether was therefore added and the flask shaken. When the reaction had proceeded for some time further, the preparation was placed on the water bath, more sodium introduced in small amounts and the whole allowed to stand several hours.

At the end of this time the action was judged to be complete and the crystals were filtered out, washed

with absolute alcohol and recrystallized from ether. About a gram was obtained of light, slender, fluffy needles of a beautiful deep red color. They were almost insoluble in alcohol, and only slightly in ether, but proved somewhat more soluble in benzol. At 270° they darkened somewhat, but did not melt below the boiling point of sulphuric acid. They were later found, on careful examination with a lense, to consist of two compounds intimately associated, one of which had lent the color and the other the crystal form to the mixture. The red compound was very finely divided and apparently amorphous, while the colorless or light colored substance crystallized in branching needles. They were separated by recrystallization from benzol, the white ones being the more soluble. These were unfortunately spilled and lost before the end of the operation. The red compound resulting did not melt below 350° C., and was analyzed for Bromine as follows:-

Determination of Bromine - 1st Red Compound.

Carius' Method. (1 gram AgNO_3)

Weight Substance and Tube	1.8698	
Weight tube	<u>1.6701</u>	
Weight Substance	.1997	
Weight crucible + AgBr	6.5260	
Weight crucible	<u>6.3458</u>	
Weight AgBr	.1802	
Weight Br.	.0767	
Percent		38.4
Percentage Bromine	38.4	
Later determination	37.56	
" "	36.60	
Miss Thomas' Analysis	43.64	

Experiment 2.

The 25 grams of oil, from the 3rd Preparation of the dibromide, was treated in a similar manner to the preceding experiment, with similar results. Thirty grams of sodium were used, and about 100 c.c. of alcohol. A small amount of a fine white precipitate deposited during the reaction, and was found to be soluble in water and alcohol. About 3 grams of the red compound were obtained, which appeared lighter than the previous preparation in color, but did not melt below 350°C. , and had the same solubility. The substance was recrystallized a large number of times from benzol, and was separated by this process into two portions of different shades, of which the darker was the less soluble. About a liter of solvent was used in each case, and this dissolved only a fraction of a gram of substance. The darker batch had the same color as the preceding preparation, and the lighter was therefore tested for bromine as follows:-

Bromine Determination - Lighter Red Compound.

Weight substance and tube	1.9211	
Weight tube	<u>1.6685</u>	
Weight substance	.2526	
Weight crucible + AgBr	6.5351	
Weight crucible	<u>6.3141</u>	
Weight AgBr + glass	.2210	
Weight glass	<u>.0040</u>	
Weight AgBr	.2170	
Weight Br	.0924	
Percent		36.6

Experiment 3.

The 7 grams of $C_{14}H_{10}Br_2$ crystals, from the 2nd Preparation of the dibromide, were dissolved in 50 c.c. of absolute alcohol and 10 grams of sodium slowly added. The reaction was violent, and the solution turned first milky white and later a chocolate color. No precipitate formed during the reaction, nor on standing, several hours. After a number of days the solution turned red and deposited on slow evaporation in the air, first a red solid and later a red oil, both of which were mixed with a solid mass consisting of unknown quantities of sodium ethylate and its decomposition products NaOH and Na_2CO_3 . The precipitate was thoroughly washed with water to remove these latter, and the oil dissolved in ether, leaving a few hundredths of a gram of red solid, which was recrystallized from the same solvent. Solid and oil were similar in properties to those of the preceding experiments.

Experiment 4.

The 17 grams of partially solidified oil, from the

5th Preparation of dibromide, were dissolved in 25 c.c. of abs. ether and 125 c.c. of abs. alcohol and treated with 10 grams of finely cut sodium, the flask being placed in ice to prevent evaporation of the solvents. The solution immediately changed from deep yellow to rose color and finally to a dull brown. On standing over night the red compound deposited, and was removed and washed with alcohol and ether. A slight precipitation continued for several days, from which the solution was decanted at intervals, until finally the deep red oil appeared. The oil was removed and washed with water and the red solid recrystallized several times from ether. Yield 1.2 grams of solid and 15 grams of oil. Solid and oil similar to preceding preparations, solid having the same shade of color as that first prepared. The solid was analyzed for bromine as follows:-

Determination of Bromine - 3rd Red Solid.

Weight of substance and tube	1.8610	
Weight tube	<u>1.6688</u>	
Weight substance	.1922	
Weight crucible + AgBr	6.7155	
Weight crucible	<u>6.5455</u>	
Weight AgBr	.1700	
Weight Br.	.0723	
Percent.		37.56
Previous determination	38.4	
" "	36.6	

Distillation of the Oil.

The 15 grams of oil, obtained from the previous experiment, were subjected to distillation, using a distilling flask having its delivery tube cut off short. Below 120° small amounts of water passed off, with much snapping and crackling. The thermometer then rose rapidly to 340° and a gray vapor appeared, which was partly HBr. After a few minutes, the oil began to pass over, giving a liquid distillate at first, but later one which immediately solidified, the temperature rising to 360°. It was decided from the fumes of HBr that the high boiling oil was being largely decomposed and the operation was discontinued.

A later attempt was made under diminished pressure, keeping the flask at about 35 m.m. A small amount of water again appeared, with a similar disturbance, which in this case increased until the liquid was bumping with great violence, and part had been thrown into the side tube. A portion of the distillate having also solidified in this tube, the distillation was stopped and the mass

removed. Fumes of H Br were given off during the distillation, and it was noted that the contents of the flask, which was red at the beginning of the experiment had changed to brown. On continuing the process, the tube again choked up rapidly and it was again necessary to stop the distillation and clean it. The pressure was kept at about 35 m.m. as before, H Br being also given off and the thermometer registering 195-200°. On attempting a third time to continue the process, the bumping, which at no time had been absent, became of such exceptional violence that it was useless to continue the distillation. Glass beads were tried without success and the entire method therefore given up.

This attempt under vacuum having proved unpleasantly troublesome, the distillation was again tried at atmospheric pressure. Possibly due to the fact that all water had finally been removed, no bumping was experienced, and the liquid passed over quietly between 335 and 350°, giving off large volumes of H Br. The distillate was a light brown oil, which solidified to a dark yellow mass.

On recrystallizing, clusters of yellow needles were obtained, melting at 63°. These were undoubtedly the 10 monobrom phenanthrene.

Treatment of the Bromine Compounds with
Sodium Ethylate.

Experiment 1.

The detailed notes of this work have been lost. It is known, however, that the 10 grams of $C_{14}H_{10}Br_2$ from Preparation 4, or the 17 grams of oil or both, were treated with methyl alcohol and sodium in much the same way as the previous experiments. A red oil was obtained, but no red solid or other compound of interest.

Experiment 2.

The crystals of 10 monobrom phenanthrene, obtained by distillation of the oil produced in Experiment 4, just described, were treated with methyl alcohol and sodium methylate. Five grams of the substance were used, and the equivalent of a molecule of sodium methylate dissolved, in 100 c.c. of absolute methyl alcohol. The solution was allowed to stand two days, warming to the boiling point at intervals. It was then evaporated slowly to dryness, and washed with water to remove sodium hydroxide and carbonate.

On recrystallization of the residue from alcohol, it was found to be unchanged 10 brom phenanthrene. The wash water was neutralized with dilute HCl and evaporated to dryness, small amounts of oil depositing and being removed. On extracting the solid mass with ether, a slight amount of oily monobrom phenanthrene was further recovered, but no new compound was obtained and no red color developed during the experiment.

Treatment of 10 Brom Phenanthrene to Produce
Higher Bromides.

The 18½ grams of 10 C₁₄H₉Br, from Preparation 6 of the dibromide, were dissolved in carbon disulphide and two molecules of bromine added. The mixture was heated in a flask with a reflux condenser for two days, and, as part of the bromine was vaporized, small amounts were added at intervals. A dark colored viscid oil was obtained, which deposited crystals on standing. The crystals were filtered from the oil by suction, and, on recrystallization, yielded 8 grams of silky, yellowish-white needles, which melted at 187°. These were very probably the tetrabrom compound described by Zetter, and melting at 185°. Twenty grams of oil remained.

Treatment of Phenanthrene in Solution to Produce
Higher Bromides.

Fifteen grams of phenanthrene were dissolved in 60 c.c. of carbon disulphide, and heated with 45 grams (or 6 molecules) of bromine for three days, in a flask with a reflex condenser. At the end of this time, the HBr fumes had ceased to be given off, and there remained in the flask a dark brown viscid oil. On removing the contents to a crystallizing dish, and allowing to stand several days, fine crystals appeared throughout the mass, and these were separated by long suction with a filter pump. A second crop deposited on longer standing, and was similarly removed, and both products recrystallized from carbon disulphide. $1\frac{1}{2}$ grams were obtained of large, yellow, diamond shaped tables, which melted at 158° . These are the dibromide, $C_{14}H_9Br_2$, prepared by Zetter and melting at the same temperature.

Eighteen grams of oil remained, and appeared similar to those prepared by heating phenanthrene with un-

diluted bromine. On distillation, large quantities of HBr passed off, mixed apparently with small amounts of other non-condensable gases. The oil passed over at about 370°, giving a clear amber colored distillate, containing some red colored fractions, evidently as impurity. On cooling to zero degrees, the distilled oil would not solidify, and differed, in this respect, from those prepared in the preceding experiments.

Treatment of Subliming Phenanthrene with
Bromine Vapors.

In this experiment, 75 grams of phenanthrene were heated in a retort, through which bromine vapors were passed in a current of carbon dioxide. The gas was produced in a Kipp generator, and washed with concentrated sulphuric acid, being then bubbled through a carefully heated flask containing liquid bromine. The retort was sharply inclined, and the inlet tube was carried from the tubulature slightly into the neck, such that no substance depositing on the tube could drop back into the retort body. On passing from the receiver, which was tightly closed, the current of gas was led through wash bottles containing chloroform and sodium bicarbonate to absorb the bromine.

The operation lasted about $1\frac{1}{2}$ hours, the distillate being partly liquid oil and part oily solids, which, however, combined in the receiver to form a clear red liquid. Fifteen grams of black tarry residue remained in the re-

tort, which it was attempted to purify, without success. On filtering the benzene solution, first through paper, and then a number of times through boneblack, it still remained of a dark color and was discarded. The oil had an aromatic odor when hot, did not solidify when cooled below zero degrees, and gave no solid matter on solution in ether. It was kept, but not investigated further.

Treatment of Phenanthrene with Undiluted Bromine.

Experiment 1.

Ten grams of phenanthrene were placed in a $3/4$ inch glass tube, sealed at one end, and 5 c.c. of bromine added. The reaction was quite violent. The bromine was partially blown out of the tube, and lodged on the experimenter's fingers, - to the detriment of the fingers. Five grams of red, sticky oil were obtained, and several running sores. The oil was not treated further, attention being concentrated on the latter product.

Experiment 2.

Fifteen grams of phenanthrene were treated in an erlenmeyer flask, with 20 grams of undiluted bromine, at laboratory temperature. The reaction was vigorous, large quantities of H Br being given off, and the mass assuming a yellow color. After the addition of the bromine, the flask was heated five hours on the water bath, with a long tube as a reflux condenser, and on standing overnight, the contents had the appearance of a thick, dark-colored

liquid. The preparation was then heated eight hours further, during which time small amounts of bromine were added at intervals, and H Br continued to be given off. There remained on final cooling a dark-brown sticky mass, from which ether dissolved a dark-colored oil, leaving a dirty, dark yellow residue. The latter on washing and crystallization from the same solvent, yielded about a gram of light orange crystals, that did not melt below 270° .

The larger amount of ether was distilled from the oil, and the remainder allowed to evaporate in the air, thirty grams of a red-brown, very sticky liquid being obtained. It was very soluble in ether, but only slightly soluble in alcohol, benzene, and lingrain. On distillation part passed over 370° , with evolution of H Br, but much remained as a charred mass. The distillate was a yellow oil, which did not solidify at zero degrees.

On further recrystallization of the orange crystals from benzene, there resulted a mixture of large

white prisms and smaller yellow needles. The former appeared to rapidly lose benzene of crystallization, and crumbled to powder. These were partly separated mechanically, and dissolved in chloroform. On evaporation, this solution was accidentally allowed to go to dryness on an asbestos pad, and it was noted with great interest, that instead of a white residue remaining, there appeared in the dish a fluffy mass of small, delicate, dark-red needles. To further investigate this change, the melting point of one of the few remaining white crystals was tried, and it was found to turn gradually red without melting, at about 300°.

The residue of yellow needles was again recrystallized, this time from chloroform, in order to recover as much of the white crystals as possible. A small quantity of these was obtained, and was separated mechanically with much care. On trying a melting point, they also turned red, which proved them identical with the preceding. Examined with a lense, the white crystals were seen to be very definite hexagonal prism, the basal pinacoid appear-

ing as plain as in a crystal model. A very small quantity only of both compounds was obtained.

Experiment 3.

Fifty grams of phenanthrene were placed in an erlenmeyer flask, and 75 c.c. (or about 10 molecules) of bromine added in small amounts, during an interval of 15 minutes, the operation being carried on at laboratory temperatures. The reaction was very violent, great quantities of hydrobromic acid passing off, and much bromine vapor. The flask was then allowed to stand two hours, with occasional agitation, at the end of which time the contents had the appearance of a thick, red liquid, and the reaction had diminished to a slow regular evolution of gas. It was then placed in the sunlight outside the laboratory window for two days, being taken inside during the night. The temperature was below freezing. At the end of this period, the contents had become solid at inside temperature, and the flask was gently heated for several hours until the slight remaining traces of bromine and H Br were removed. On cooling, a transparent,

deep red solid of a resinous appearance remained.

On treating this solid mass with carbon tetrachloride, a red oil dissolved leaving 28 grams of a granular, orange yellow residue, of lesser solubility. The latter, on three recrystallizations from tetrachloride, gave a yellowish white product without definite crystals, melting at 190-198°. The filtrates from the crystallizations were a much deeper yellow, and the top pieces of the solid turned yellowish rapidly on exposure to air and sunlight. It was very slightly soluble in alcohol, but dissolved sparingly in benzene and somewhat more easily in chloroform and carbon tetrachloride. The solubility in the latter two was much increased on heating.

A systematic purification of the compound was next begun. The method adopted was that of boiling a small quantity with much C Cl_4 in a large distilling flask, adding more solvent until it dissolved, and then distilling until the compound showed signs of precipitation, finally pouring out into a large crystallizing dish to cool and crystallize. After several treatments of this sort, a

white compound was obtained, which melted at 226-228°.

The preparation was now at a standstill for six months. At the end of this time, the clear, red, syrupy oil which had remained from the original solution in carbon tetrachloride, had become brown and opaque and deposited a granular solid. By careful treatment with a small amount of carbon tetrachloride, 10 grams more of yellow compound was obtained, similar to that first prepared. The recrystallization of the partially purified white compound was also continued, using the same method described above. Its melting point finally became constant at 235°. The compound crystallized in long silky fibres, which matted together on the suction plate, and was pure white, and did not oxidize yellow on standing. It was very slightly soluble, if at all, in methyl and ethyl alcohols, somewhat more soluble in ether, and only sparingly in benzene, chloroform and carbon tetrachloride. A liter of the latter two solvents dissolved when hot, not more than three or four grams. About two grams of solid

were obtained.

A bromine determination was made by Carius' method on the portion melting at 235° , as follows. The first two tubes prepared exploded in the furnace, about 0.4 gram of substance being lost.

Determination of Bromine - White Solid.

Weight tube + substance	2.3202	2.3266
Weight tube	<u>2.1316</u>	<u>2.1540</u>
Weight Substance	.1886	.1726
Weight Cruc. + AgBr	10.4710	11.8072
Weight crucible	<u>10.1784</u>	<u>11.5432</u>
Weight AgBr	.2926	.2640
Weight bromine	.1245	.1123
Percents.	66.02	65.05
Calculated for $C_{14}H_6Br_4$		64.80
" " $C_{14}H_5Br_5$		69.82

The compound is therefore a tetrabromide.

The purification of the remaining fractions of material was next attempted. These consisted of the obtained tetrabromide, with probably isomers and lower bromides, and with some possibility of bromine addition products. In appearance, as the impurity increased, they changed from silky fibres to mixture containing fibres and increasing quantities of granular flocks of fine needles, and finally graded from the latter into non-crystalline grains. In recrystallization, the previously described method was used, and the filtrate from the purer fraction was taken in each case to dissolve the next in purity, and the process continued down the list. Two or three small batches of pure tetrabromide were prepared. When the work was discontinued, melting points were taken of the different remaining fractions, which are as follows,

1. Pure $C_{14}H_6Br_4$

Properties given above. Melts at 235°.

2. Fairly Fibrous. White.
Oxidizes slightly
Melts and decomposes at 222-223°
3. Less Fibrous. Faint Yellowish.
Oxidizes slightly yellow
Melts and decomposes to a red liquid at 212-213°
Liquid does not solidify.
4. Adherent, but not fibrous - Yellowish
White.
Oxidizes strongly yellow on corners.
Melts and decomposes to red liquid at 195-202°
5. Separate Flocks. More Yellow.
Oxidizes yellow.
Melts without decomposition at 180-185°
Liquid solidifies readily.
6. Grains. Very dirty yellow.
Melts without decomposition at 171-178°
To red oil which does not solidify
7. Red, clear, viscous and sticky oil
Six months later had solidified to
a sticky, yellow mass.

Research Publications upon

Brom, Methoxy, Ethoxy and Hydroxy Phenanthrenes.

Fittig and Ostermayer. Ann. 166. p. 361.

Dibromide.

Hayduck. Ann. 167. p. 177.

Dibromide, Monobrom, Dibroms 2, Tribrom.

Zetter. Ber. 11. p. 164-173.

Dibromide, Monobrom, Dibrom 2, Tribrom.

Tetrabrom, Hexabrom.

Limprecht. Ber. 6. p. 532.

Dibromide, Monobrom, Dibrom, Tribrom.

Schmidt, Metzger and Junghaus. Ber. 40. p. 4240.

2-7 Dibrom, 2-7 Dibrom Quinone, 2 Brom Quinone.

Ber. 41. p. 4215.

10 Hydroxy.

Schmidt and Scherer. Ber. 44. p. 740.

10 Hydroxyquinone.

Werner. Ann. 321. p. 248.

10 ? Dibrom, 2 Hydroxy, 3 Hydroxy, 10 Hydroxy.

2 Methoxy, 3 Methoxy, 3 Ethoxy, 3 Methoxy quinone.

Ann. 322. p. 155.

2 Hydroxy Quinone, 3 Hydroxy Quinone, 2 Methoxy Quinone, 2 Ethoxy Quinone, 1 Brom Quinone.

Pschorr - Wolfs and Buckow. Ber. 33. p. 162.

1 Methoxy, 2 Methoxy, 1-5-6 Trimethoxy, 3 Methoxy Quinone, 1-5-6 Trimethoxy Dibrom, 6 Hydroxy, 1-5 Dimethoxy.

Pschorr - Sumueleau, Jaeckel and Buckow. Ber. 33, p. 1810-26.

3 Hydroxy, 3-4 Dimethoxy, 3-4 Dimethoxy, Dibrom.
3 Hydroxy, 4-Methoxy, 4-Methoxy, 4 Methoxy Dibrom.
4 Methoxy Dibrom Quinone, 2-3 Dimethoxy, 2-3 Dimethoxy Quinone, 2-3 Dimethoxy Dibrom, 2-3 Dimethoxy Dibrom Quinone.

Pschorr - Seydel. Ber. 34. p. 3998.

2 Hydroxy, 2 Methoxy, 3 Methoxy Dibrom.

Pschorr - Busch. Ber. 40. p. 2001.

1-5-6 Trimethoxy.

AN ELECTRIC FURNACE FOR COAL ANALYSIS.

A Thesis submitted to the faculty of the Graduate
School of the University of Minnesota by
Charles Royal Cressy
in partial fulfillment of the require-
ments for the degree of
Master of Science.

May 1912.

INTRODUCTION.

The determination of volatile matter in coal, in spite of the standard methods almost universally employed, is one which the different chemists check each other with much more widely varying results than is common in other classes of analytical work. As is well known, this is largely due to the fact, that the hydrocarbons, of which the volatile matter is composed, do not exist primarily as such, in a definite percent in the coal, but are rather produced by the decomposition, during its ignition of certain other, more or less unknown, and more complex hydrocarbons originally present, and that further, the amount and character of this decomposition varies with the temperature and duration of the heat, and with the percentage of moisture and other factors.

The Standard Method, most widely used, calls for a platinum crucible weighing 20-30 grams and having a well fitting cover, and specifies that the time of ignition be exactly seven minutes, and that the bunsen flame be 20 mm.

high and the crucible set 6-8 mm. above the top of the burner. Many rather large variations have been found in the percentages of volatile matter reported, when different individual chemists have analysed the same coal sample by this method, from which it is evident that the differences in the smaller details of circumstances and manipulation are sufficiently serious to affect at least the amount of volatiles driven off, within the limits of accurate quantitative results, if not also their character and composition.

In the hope of remedying these difficulties many variations of this and other procedures have been tried, but without having developed, at present, either an ideal or a satisfactorily accepted method, and it has been occasionally suggested that with a small electric furnace the temperatures could be more easily regulated and other conditions more readily standardized than with any of the other types of gas or muffle heating.

With these suggestions in view, which were made originally to the writer by Dr. Geo. B. Frankforter, this research was begun under his direction. It was aimed to

produce a suitable electric furnace, prepare a sufficient³ number of properly graded coal samples and to run through a large number of determinations of volatile matter upon each one, varying at the same time such conditions, in the different series of analyses, as would appear advisable, in order to discover the best and most accurate method of procedure.

Objections to the Standard Method.

Some of the possible causes of the discrepancies which result when the Standard Method is employed, may be set forth under several different headings as follows:-

A - The Burner.

1st. The heights of the bunsen flames used, may be different. The tip of the flame is often almost colorless and hard to distinguish accurately.

2n. The size of the flames may vary. A broader flame, due to a larger bunsen tube, will subject the crucible to a higher temperature, and the speed with which it attains this temperature, on being placed in the flame, will be greater.

3d. The rates of gas consumption may vary. Larger gas openings at the base or a wider opening of the gas cock may be compensated by adjusting the air holes to give the required height. The flame then burns with a higher temperature and gives off a larger number of heat units per second.

4th. The composition of the gas may be different. It may have a higher calorific power or give a higher temperature. The effect is similar to the preceding higher speed of combustion.

5th. The flames may not be properly protected. Without a suitable shield, and with draughts in the room, the flame may be blown to one side of the crucible, to the obvious detriment of the results. Failure on the part of the analyst to place the crucible in the exact center of the flame is a serious defect.

B - The Crucibles.

1st. Apart from differences in weight, these may not have the same size, shape, or thickness. The size and shape regulate both the depth of the layer produced by the

specified one gram of coal, and the volume of the confined space above it. A thinner body of coal will have a larger surface exposed to the hot bottom of the crucible and will give a speedier upward conduction of heat to the top layers of its mass, and, by reason of this, a more rapid attainment of the maximum temperature, and more rapid completion of the distillation period. The larger upper surface, also, and lessened mean distance which the volatiles must travel within the coking mass, will have the same effect of accelerating the discharge of the vapors, and as has been mentioned, the temperature and rate at which these are liberated influence their quantity and composition. The amount of confined space above the coal probably has a definite effect of some character upon the final results, but if so, the details of this are obscure, at least to the author. If higher hydrocarbons are cracked upon the walls of the crucible and deposit soot, this is probably burned off in the latter part of the ignition. The thickness of the crucible, also, is of less importance and has to do with the conduction of heat from flame to coal.

2d. The covers of the crucibles may not fit with uniform tightness. This may vary even with the same crucible in different determinations. Looser fitting, within limits, will allow the volatiles to escape more rapidly and with less pressure or choking. Moderately wide openings may even allow entrance of air towards the end of the process, burning away varying quantities of soot or coke. Greater pressure may compel the volatiles to remain longer within the crucible, where they suffer greater chances of decomposition and hinder the proper evaporation of their successors from the coal.

C - The Time.

Different chemists may not measure this with the same degree of exactitude. With a longer time more coke or deposited soot may be burned away.

Advantages of an Electric Furnace.

In considering the points of superiority of the electric furnace as contrasted with the foregoing, only part of the difficulties will be seen to be ameliorated. The size and shape of the crucible and the time of ig-

nition must be regulated with the same care in both methods, at least when the electric furnace remains open to the air. On the other hand the difficulties having to do with the temperature and rate of heat liberation are to a very large extent removed, and as these are the ones to which the errors are most largely attributed, the method shows a corresponding improvement. It must not be forgotten, however, in this connection, that if a standard method is finally to be developed, the dimensions and material of such a furnace, as well as of the crucible, should be very accurately standardized by some national committee. It should then be carefully manufactured in this form, probably by one firm of makers only.

Some of the most obvious advantages may be discussed as follows:-

1st. Electrical energy is much more easily controlled, and measured with accuracy, than heat from gas or other flames. Suitable ammeters, voltmeters and resistances are of course necessary and likewise expensive. The measure of the electrical energy is the measure of

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the heat liberated, and, as there are no products of combustion or admixed air to vary and interfere, as in the gas flame, the temperature, upon attaining its maximum, will have a tendency to remain uniform and constant, with a steady electric current. This will be true for the same or an identically manufactured furnace. All the variations moreover, of flame height, size, and position with respect to the crucible are done away with, and there can be no blowing away of a flame from around the crucible due to draughts. Instead of these there are substituted only, the proper placing of the crucible within the furnace and the simple current measurements, with perhaps pyrometer readings occasionally as a check. In other words, all these standardizations, which are at present difficult and left undone by analysts, would be done, in effect, once for all, in manufacturing the furnace according to specifications.

2d. An additional point is the fact that the atmosphere around the crucible is more accurately controlled. In the first place, it is free from the variable oxidizing and reducing action and water vapor of the bunsen flame. In the second, with a covered furnace, a current of an

inert gas may be used, doing away with all oxidizing effects and facilitating the removal of the vapors. It must be mentioned, however, that any more volatile soot, that might be cracked or deposited upon the crucible, will not be burned away, which is a possible, though doubtful advantage. Finally, with direct heating types of furnaces, having the crucible in contact with the heating elements, the use of vacuum or at least diminished pressure is a possibility that is worth experimental work.

Description of the Furnace.

In its larger proportions, the electric furnace prepared for these investigations consisted, as is shown by the drawing, in a wire-wound porcelain crucible set in a covered brass cup, the latter being provided with tubes for the entrance and exit of a current of gas. The crucible B was a special type about 5 cm. high made with straight sides for the greater part of its length, and with a rim at the top that curved outward at right angles for a few millimeters. It was wound with fine platinum wire, and covered over with numerous segments of asbestos paper, which in turn were tied in position by further separate

lengths of the wire. The coil necessary for heating the bottom was covered with two asbestos paper discs and clamped in position by a small perforated porcelain plate taken from a gooch crucible. To this the end of the side winding was also fastened and it was held rigidly in place by several very heavy wires that ran diagonally from holes at its edges to the top of the crucible and were there wound and firmly attached together to form a thick circle of a number of strands.

The brass body A, of the furnace, was originally a large oil cup, with straight sides and a flat bottom on the inside, and with its depth and diameter about equal. There had been, when it was purchased, a narrow oil channel leading down through a thick stem from the center of its bottom, and this was bored out to a large size and the graphite plug C cemented in with water glass. This latter carried two thick walled porcelain tubes, out from the tube of a rose crucible and cemented in the same manner, and these provided entrance ways and insulation for the heating wires of the furnace. In the stem above the plug, and also in

the center of the plain brass cover, holes were further
bored and tapped to receive the short brass tubes E and F. 11

The crucible was supported by its flange, which rested upon the inner edge of a ring G of sheet copper, around the center of which a circle of holes were drilled to allow the exit of air and flow of gas from the bottom of the furnace. This in turn was supported by a slit cylinder H, of the same material, which dropped in and fitted snugly to the inside of the cup, and a circle of stiff brass wire was further bent and pushed down against the ring, to hold the two firmly in place in case the apparatus be inverted. The sides of the furnace were protected from the heat of the crucible by a number of coils of asbestos paper, which were placed both between the cylinder and the sides, and the cylinder and the crucible. The remaining space was then filled with the more fluffy variety of asbestos fibre.

Discussion of the Work.

After the preparation and finishing of the furnace, which included several trial heatings of the wound crucible before placing in the cup, the apparatus was tested as to the rate of temperature rise and rate of cooling, and a preliminary analysis made of volatile matter and ash on one sample. Following this, a series of determinations of volatile matter was begun, upon each, in turn, of ten previously prepared coal samples, only three of which were finally completed.

A special platinum crucible was used, which was higher and narrower than the common type and fitted better the porcelain crucible forming the heating element of the furnace. An ordinary cover being inadvisable, owing to its projecting lip, a special cover had also to be made, and this was hammered out of heavy platinum sheet and had the shape of the common porcelain cover, with a ring of platinum wire fastened through a hole in its center. In order to test the effect of an air space between the crucible and furnace upon the uniformity of heating, a

platinum wire basket was further made, which had suitable rings to uphold the crucible and also projecting parts to keep it equidistant from the sides and bottom of the furnace.

The ten coal samples mentioned were prepared for analysis by grinding to pass through first 100 mesh and then bolting cloth, and by a thorough subsequent mixing on oil cloth sheets. Nine of these, of varying volatile matter and moisture, were taken from the Quantitative bottles and the tenth, which is Sample I, had been previously analyzed by the writer and prepared in the same manner. Before beginning the analyses, all the samples were kept two weeks in a fresh calcium chloride desiccator and the weighing bottles containing them were also returned to this immediately after each weighing, which in each case was timed to occupy exactly two minutes. Gram samples were used throughout the work.

At the beginning of the tests, determinations were made according to two different styles of procedure, the first being to place the crucible containing the sample

in the cold furnace and heat both up together, and the ¹⁴
second, to introduce the crucible into the furnace, after
it had reached the maximum temperature produced by the
current used. In this latter case, however, explosions
were frequent, and the method was omitted on the last two
samples. The wire basket, also, appeared to give slightly
better results, and sample three, in the order of analysis,
was ^{run} entirely in that manner. It should be noted that the
furnace heats up very rapidly and cools at a fair rate,
such that the platinum crucible reaches its maximum tem-
perature to the eye in $1\frac{1}{2}$ minutes and cools again in
3 minutes. The furnace cover was not used in any of the
tests.

The following tables give a resume' of the more
important results.

Table 1 - Analyses by Standard Method.Analyses by the Writer.

Sample No.	Moisture.	Volatils.	Fixed C.	Ash.	Vols. and Moisture.
150	1.28	33.84	60.73	4.14	35.12
148	3.06	33.09	51.11	12.74	36.15
I	4.08	43.53	39.01	13.47	47.53

Averages of Analyses from Quantitative Laboratory Reports.

Sample No.	Moisture.	Volatils.	Fixed C.	Ash.	Vols. and Moisture.
150	1.2	33.5	61.1	4.2	34.7
148	3.8	30.6	52.1	13.5	34.4

Table 2 - Furnace Analyses.

SAMPLE No. 150.		(Standard Method 35.12) (Quantitative Average 34.7)			
Cold Start - Crucible in Contact.					
Number.	Ave. Amperes.	Volts.	Time - Mins.	Percent.	
1.	6.2	118	4	35.87	
2.	6.8	116	4	35.70	
3.	6.7	115	4	35.48	
4.	6.8	116	4	35.52	
5.	7.1	113	4	35.67	
Cold Start - Wire Basket.					
6.	6.1	115	7	35.63	
7.	6.5	115	7	35.01	
8.	5.7	114	7	35.57	
9.	7.3	114	4	35.60	
10.	7.2	108	4	35.58	
Hot Furnace - Cruc. in Contact.					
11.	6.7	115	4	Explosion.	
12.	6.6	114	4	35.60	
13.	6.7	110	4	35.53	
14.	6.9	114	4	Explosion.	
Hot Furnace - Wire Basket.					
15.	6.2	114	4	Explosion.	

Table 3 - Furnace Analyses.

SAMPLE No. 148.

All from the Cold.

(Standard Method 36.15)
(Quantitative Average
34.40).

Crucible in Contact.

Number.	Ave. Amps.	Volts.	Time.	Percent.
1.	7.2	104	7	36.73
2.	6.6	116	7	36.84
3.	6.3	120	7	35.39
4.	6.9	109	4	36.81
5.	6.8	115	4	36.62
Wire Basket.				
6.	6.8	117	7	36.78
7.	6.5	105	7	36.63
8.	6.6	109	7	36.72
9.	6.7	114	7	36.70
10.	6.7	112	7	36.65

Table 4 - Furnace Analyses.

SAMPLE No. 1.

All Wire Basket - From the Cold.
All 4 minutes - New Winding.
(Standard Method 47.53)

Number	Ave. Amps.	Ave. Volts.	Percent.
1.	6.5	114	47.35
2.	6.3	117	47.31
3.	6.7	110	47.43
4.	6.3	119	47.36
5.	6.6	115	47.34
6.	6.6	113	47.45
7.	7.1	109	47.29
8.	6.8	108	47.34
9.	6.4	117	47.38
10.	6.7	115	47.44

In discussion of these foregoing tables there is little to be said, except to mention that the determinations check each other rather nearer than is common with the Standard Method, and it is therefore proven, as has never been especially doubted that the same individual chemist can use an electric furnace for his own work and get good check results. This is obviously the first and easiest, but not therefore the less necessary point, which must be determined in order to produce an ideal method for the use of different individual chemists. The rest of the proof, as has been previously mentioned, demands extensive cooperation.

This particular furnace, however, although it gave good results while it lasted, was not by any means ideal in this "last" respect. Due to expansion with the rise in temperature, the wires loosened easily from the porcelain crucible in places near the bottom where the sides curve in at a slight angle, and burned out twice in this vicinity, necessitating tedious rewinding. At the end of Sample I a third burn-out finally convinced

both Dr. Frankfarter and the writer that further endeavor was useless until a perfectly straight crucible could be found, and as this occurred shortly after the close of the school year and the writer then left to engage in permanent business in another city, the continuation of the investigation was indefinitely postponed. It should be mentioned at this point, that during the time which has elapsed since this work was carried on, several small electric furnaces, expressly designed for the heating of crucibles, have been put upon the market by at least two concerns, one of these being the Hoskins Co. No general attempt, however, has yet been made to develop a standard method for volatiles in coal by their use.

DETAILED EXPERIMENTAL PARTANALYSIS OF COAL - STANDARD METHOD.

SAMPLE No. 150.

Moisture.

16.5544	15.8456	
<u>16.5419</u>	<u>15.8324</u>	
.0125	.0132	Ave. 1.28%

Ash

15.5957	14.8872	
<u>15.5544</u>	<u>14.8556</u>	
.0413	.0416	Ave. 4.14%

Volatiles and Moisture

(Same Cruc. as in Hl. Furnace Analyses)

9.8330	9.8328	
<u>9.4812</u>	<u>9.4821</u>	
.3518	.3507	Ave. 35.12%

Volatile Matter.

.3393	.3375	Ave. 33.84%
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Fixed Carbon.

.6069	.6077	Ave. 60.73%
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ANALYSIS OF COAL - STANDARD METHOD.

SAMPLE No. 148

Moisture.

16.1528	15.2402	
<u>16.1225</u>	<u>15.2094</u>	
.0303	.0308	Ave. 3.06%

Ash.

15.2800	14.3678	
<u>15.1528</u>	<u>14.2402</u>	
.1272	.1276	Ave. 12.74%

Volatils and Moisture. (Same Crucible)

9.8331	9.8332	
<u>9.4714</u>	<u>9.4720</u>	
.3617	.3612	Ave. 36.15%

Volatils.

.3314	.3304	Ave. 33.09%
-------	-------	-------------

Fixed Carbon

.5111	.5112	Ave. 51.11%
-------	-------	-------------

ANALYSIS OF COAL - STANDARD METHOD.

SAMPLE No. I.

Moisture.

15.8382	16.8323	
<u>15.7972</u>	<u>16.7918</u>	
.0410	.0405	Ave. 4.08%

Ash.

14.9726	15.9673	
<u>14.8382</u>	<u>15.8323</u>	
.1344	.1350	Ave. 13.47

Volatils and Moisture.

21.5984	21.5982	
<u>21.1236</u>	<u>21.1225</u>	
.4748	.4757	Ave. 47.53

Volatils.

.4338	.4352	Ave. 43.45
-------	-------	------------

Fixed Carbon.

39.08	38.93	Ave. 39.01
-------	-------	------------

PRELIMINARY HEATING OF FURNACE.

Without cover.

I. Without Crucible.

Time - seconds	Amperes.	Heat.
0	0	Cold.
	30	Porcelain dull red near top
	60	All crucible medium red.
	75	Bright red, yellow, maximum intensity.
	5 mins.	" " "
	5.9	" " "

II. With Crucible - Cover off.

Time - seconds.	Amperes.	Heat.
	0	Cold
	20	No red.
	30	Faint red above crucible.
	45	Bright " " "
	60	Crucible dull red
	75	" bright "
	90	" " yellow
	--	" " "
	3 min.	" " Brass very hot.
	5.9	" " "

When kept at 3 amperes - Barely perceptible red.

PRELIMINARY HEATING OF FURNACE.

II. With Crucible-Wire Basket - Crucible cover off.
118 volts.

Time - Sec.	Amperes.	Heat.
0	7.8	Cold
15	6.9	No red.
30	6.2	Perc. dull red above cruc.
45	6.1	" bright " " "
60	6.0	Platinum dull red.
75	5.95	" bright "
90	5.9	" bright yellow - maximum.
3 mins.	5.9	Brass snaps to touch - tube cool.
5 "	5.85	Side Tube " " "
7 "	5.7	"

Much smoke from asbestos.

Cooling - from Sample No. 150 No. 1.

	30 secs.	Crucible cov.	dull red.	Crucible bright red.
1		"	" very dull	" " "
1	30	"	cold	" red
2		"	"	dull red
	30	"	"	" very dull
3		"	"	" Bottom cold.

PRELIMINARY ANALYSIS.

SAMPLE No. 150. - Porcelain cover on Crucible.

Volatils.			116 Volt.
Time - Min.	Sec.	Amperes.	Heat and Volatils.
	0	7.8	
	45	7.1	
1		6.1	Volatils: begin
3	30	6.0	Volatils: end
7		6.0	

Shreds of Vol. Matter on Cover.

Percentage Volatils.

9.8340
9.4822
 .3518

35.18%

ASH

(Separate sample)

Ran 5 minutes at 3 amperes and 15 min. at
 6 amperes.

8.8745
8.8334
 .0409

4.09%

SAMPLE No. 150, No. 1.

29

From the Cold Crucible in Contact - Time 4 min.

Time.	Amperes.	Heat.	Volatiles.
Hr.Min.Sec.			
Start. 4 40 0	8.00	Red through holes	
15	7.00	Red through holes	
30	6.80	Porc. slight red.	
45	6.20	Porc. red	Commence.
41	6.10	Porc. bright red	Heavy.
30	6.05	Porc. " yellow	"
42	6.00	" " "	Catch fire.
30	5.95	" " "	Cease.
43	5.90	" " "	No Vols.
30	5.90	" " "	"
Stopped 44	5.90	" " "	"

Cooled 3 minutes.

Volatiles on Crucible and Cover - Slight on Cruc. None on Cover.

Voltage 118

Percent. Volatiles

9.8335

9.4748

3587

35.87

SAMPLE No. 150, No. 2.

30

From the Cold Crucible in Contact - Time 4 min.

Time			Amperes.	Heat and Volatiles.
Hr.	Min.	Sec.		
Start.	10	31 0	8.60	
		15	7.80	
		30	7.15	
		45	7.05	Vols. begin.
	32		7.05	Vols. continue.
		30	7.00	"
	33		6.90	Catch fire
		30	6.80	Cease
	34		6.50	No.Vols.
		30	6.25	"
Stopped	35		6.20	"

Cooled 3 minutes
Volatiles - Slight on inside Crucible - none on
Voltage 116 Cover.
Percent. Volatiles.

9.8330
9.4760
0.3570

35.70%

SAMPLE No. 150, No. 3.

31

From the Cold Crucible in Contact - Time 4 min.

Time.			Amperes	Heat and Volatiles
Hr.	Min.	Sec.		
Start.	11	15	0	8.80
			15	7.45
			30	7.15
			45	7.00
	16		6.95	Vols. begin
			30	" continue
				"
	17		6.60	" catch fire.
			30	6.40
	18		6.40	" cease.
			30	6.30
Stopped	19		6.30	

Cooled 3 minutes.

Volatils on Crucible and Cover.

Slight on inside of Crucible - none on cover.

Voltage 115

Percentage Volatils

9.8330

9.4782

.3548

35.48%

SAMPLE No. 150, No. 4.

32

From the Cold Crucible in Contact - Time 4 min.

	Time.			Amperes	Heat and Volatiles
	Hr.	Min.	Sec.		
Start.	2	10	0	8.6	
			15	7.5	
			30	7.2	
			45	7.0	Vols.begin.
	11			6.8	Heavy Vols.
			30	6.7	"
	12			6.7	Catch fire
			30	6.6	Vols. cease.
	13			6.6	
			30	6.5	
Stopped	14			6.5	

Cooled 3 minutes.

Volatiles on Crucible and Cover.

Slight on inside of Crucible - None on Cover.

Voltage 116

Percentage Volatiles

9.8333

9.4781

.3552

35.52%

SAMPLE No. 150 - No. 5.

33

From the Cold Crucible in Contact - Time 4 min.

	Time			Amperes.	Heat and Volatiles.
	Hr.	Min.	Sec.		
Start	3	36	0	9.2	
			15	8.0	
			30	7.6	
			45	7.5	Vols. begin.
	37			7.4	Heavy Vols.
			30	7.0	"
	38			6.9	Vols. catch fire
			30	6.9	Vols. cease
	39			6.9	No Vols.
			30	6.7	"
Stopped	40			6.6	"

Cooled 3 minutes.

Volatiles on Crucible and Cover - None,

Voltage 113

Percentage Volatiles

9.8335

9.4768

.3567

35.67%

SAMPLE No. 150, No. 6

From the Cold-Wire Basket - Time 7 Min.

	Time			Amperes	Heat and Volatils.
	Hr.	Min.	Sec.		
Start	2	47	0	7.2	
			15	6.1	
			30	6.0	
			45	6.0	Red through holes.
		48		6.0	Cruc. red - Vols. begin.
			30	6.0	Vols. continue.
		49		6.0	Vols. cease.
			30	6.0	Cruc. red.
		50		6.0	"
		51		6.1	"
		52		6.1	"
		53		6.1	"
Stopped		54		6.2	2

Cooled 3 minutes.

Volatils on Cruc. and Cover - None,

Coke very small.

Voltage 115 throughout.

Percentage Volatils.

9.8436

9.4773

.3562

35.62%

SAMPLE No. 158, No. 7.

35

From the Cold-Wire Basket - Time 7 min.

	Time			Amps.	Volts.	Heat and Volatiles
	Hr.	Min.	Sec.			Before 119.
Start	3	48	0	7.4		
		15		6.6	115	Red through holes.
		30		6.5	115	
		45		6.5	115	
	49			6.5	115	Vols. begin.
		30		6.4	115	Heavy Vols.
	50			6.4	114.5	"
	51			6.5	"	Vols. catch fire.
	52			5.6	"	" cease
	53			6.5	2	No Vols. Cover red.
	54			6.5	"	" "
Stopped	55			6.6	"	" "

Cooled 3 minutes.

Volatiles on Crucible and Cover - None.

Coke very small - Crucible and cover clean.

Voltage 115

Percentage Volatiles

9.8335

9.4834

.3501

35.01%

SAMPLE No. 150, No. 8. New Winding on Furnace used on this
and the analyses following.
From the Cold-Wire Basket - Time 7 min.

Start	Time			Amperes.	Heat and Volatiles.
	Hr.	Min.	Sec.		
	3	42	0	7.4	
			15	6.4	
			30	6.2	Red through holes.
			45	6.0	
	43			5.8	
			30	5.8	Red in Cruc.
	44			5.7	Vols. begin.
			30	5.6	" continue
	45			5.6	"
	46			5.6	"
	47			5.6	" Cease
	48			5.6	No Vols.
Stopped	49			5.6	"

Cooled 3 minutes.
Volatils on Cruc. and Cover - None.
Coke large
Voltage 114
Percentage Volatils.

9.8334
9.4777

.3557

35.57%

SAMPLE No. 150, No. 9.

37

			From the Cold-Wire Basket -	Time 4 min.	
Time.			Amperes.	Heat and Volatiles.	
Hr.	Min.	Sec.			
Start	12	25	0	9.2	
			15	8.0	
			30	7.7	
			45	7.5	
	26			7.4	Vols. begin
		30		7.2	" continue
	27			7.2	"
		30		7.0	"
	28			6.9	Vols. catch fire.
		30		6.9	" cease.
Stopped	29			6.9	

Cooled 3 minutes.
Volatiles on Crucible and Cover - None.
Coke large to top of crucible.
Voltage 114

Percentage Volatiles.
9.8338
9.4778
.3560

35.60%

SAMPLE No. 150, No. 10.

38

From the Cold-Wire Basket - Time 4 min.

	Time			Amperes.	Heat and Volatiles
	Hr.	Min.	Sec.		
Start	2	54	0	9.2	
			15	8.2	
			30	7.9	
			45	7.6	
		55		7.1	Vols. begin
			30	6.6	Heavy vols.
		56		7.0	"
			30	7.1	Less Vols.
		57		7.0	Vols. cease, gases burn
			30	7.0	No Vols, Cover red.
Stopped		58		7.0	" "

Cooled 3 minutes.

Volatiles on Crucible and Cover.

Inside of Crucible, slight - Cover, none.

Voltage 108

Percentage Volatiles:

9.8334

9.4775

.3558

35.48%

SAMPLE No. 150, No. 11

39

Furnace Hot - Crucible in Contact - Time 4 min.

Time.

	Hr.	Min.	Sec.	Amperes.	Volatils.
Start	3	2	0	6.8	Porcelain yellow.
			5	6.7	Vols. begin
			15	6.6	" continue.
			30	5.5	" cease
			45	6.6	<u>" Explode</u>
	3			6.6	Coal partly blown out
		4		6.7	
		5		6.8	

Voltage 115

Percentage Volatils

9.8331

SAMPLE No. 150, No. 12.

40

Furnace Hot - Crucible in Contact. Time 4 min.

	Time.			Amps.	Heat	Volatils.
	Hr.	Min.	Sec.			
Start	4	18	0	6.7	Bright yellow	
			5	6.7		Vols. begin.
			15	6.65		
			30	6.6		" catch fire
			45	6.6		
	19			6.6		19.15 vols. cease.
			30	6.6		
	20			6.6		
			30	6.6		
	21			6.6		
			30	6.6		
Stopped	22			6.6		

Cooled 3 minutes.
Volatils on Crucible, Cover, none.
Coke - Medium size.
Voltage 114
Percentage Volatils.

9.8332

9.4772

.3560

35.60%

SAMPLE No. 150, No. 13.

Furnace Hot - Crucible in Contact. Time 4 min.

	Time			Amperes.	Heat and Volatiles
	Hr.	Min.	Sec.		
Start	11	40	0	6.9	
			5	6.8	Vols. begin
			15	6.7	" catch fire
			30	6.7	" burn
			45	6.7	"
	41			6.7	"
			30	6.7	Vols. cease
	42			6.7	
			30	6.7	
	43			6.6	
			30	6.6	
Stopped	44			6.6	

Cooled 3 minutes.

Volatils on Crucible and Cover - none.

Coke - Medium size.

Voltage 110

Percentage Volatiles.

9.8333

9.4780

.3553

35.53%

SAMPLE No. 150, No. 14.

Furnace Hot - Crucible in Contact. Time 4 min.

Time				Amperes.	Heat and Volatiles.
Hr.	Min.	Sec.			
Start	5	27	0	6.9	
			5	6.9	Vols. commence - yellow color.
			15	6.9	<u>Vols. Explode.</u>
			30		
			45		
			28		

Voltage 114

Percentage Volatiles.

9.8332

SAMPLE No. 150, No. 15.

Furnace Hot - Wire Basket. Time 4 min.

Time			Amperes	Heat and Volatiles.	
Hr.	Min.	Sec.			
Start	10	10	0	6.4	Porc. bright yellow.
			5	6.3	
			15	6.3	Vols. begin.
			30	6.2	Heavy vols.
			45	6.2	"
			11	6.2	<u>Vols. Explode</u>
			12	6.1	
			13	6.1	
			14	6.1	

Voltage 114

Percentage Volatiles.

9.8334

SAMPLE No. 148, No. 1

44

All of Sample No. 148 from the bold and no carbon or
on crucible or cover.

Crucible in Contact - Time 7 min.

	Time			Amps.	Volts	Heat and Volatiles.
	Hr.	Min.	Sec.		Before 110	
Start	3	32	0	8.2	104	
			15	7.4	104	Red through holes.
			30	7.3	104	
			45	7.2	104	Vols. begin,
	33			7.2	104	" continue
			30	7.1	104	"
	34			7.1	104	" cease
			30	7.1	104	No Vols. Cover red.
	35			7.1	103.5	"
	36			7.1	104	"
	37			7.3	103	"
	38			7.3	103	"
Stopped	39			7.4	103	"

Cooled 3 minutes.

Coke - None. Coal appears as before heating.

Percentage Volatiles.

9.8334

9.4661

.3673

36.73%

SAMPLE No. 148, No. 2.

Crucible in Contact. Time 7 min.						
	Time			Amps.	Volts.	Heat and Volatiles
	Hr.	Min.	Sec.	Before 120		
Start	11	50	0	8.2	116	
			15	7.0	"	
			30	6.5	"	
			45	6.3	"	Vols. begin
	51			6.2	"	" continue
		30		6.0	"	" catch fire
	52			6.1	"	" burn
		30		6.2	"	" cease
	53			6.6	"	No Vols. Cover red.
	54			6.6	"	"
	55			6.8	"	"
	56			6.8	"	"
Stopped	57			6.8	"	"

Cooled 3 minutes.
 Coking - Very slightly coked.
 Percentage Volatiles.

9.8330

9.4646

.3684

36.84%

SAMPLE No. 148, No. 3.

46

Crucible in Contact. Time 7 min.

Time			Amps.	Volts.	Heat and Volatiles
Hr.	Min.	Sec.		Bef. 125	
Start	2	14	0	--	120
			15	--	120
			30	6.5	120½ Crucible red.
			45	6.4	" Vols. begin.
	15		6.4	"	" " continue
			30	6.3	" "
	16		6.2	"	" "
			30	6.2	" 16.45 "
	17		6.1	"	" Vols. cease.
	18		6.3	"	" Cover red.
	19		6.3	"	" "
	20		6.3	"	" "
Stopped	21		6.2	"	" "

Cooled 3 minutes.

Coking - very slightly coked.

Percentage Volatiles

9.8333

9.4794

.3539

35.39%

SAMPLE No. 148, No. 4.

47

Crucible in Contact. Time 4 min.

Start	Time			Amperes	Volts. Before 114	Heat and Volatiles
	Hr.	Min.	Sec.			
	4	50	0	8.2	---	
			15	7.4	---	
			30	7.2	108	
			45	7.0	"	
	51			6.8	"	Vols. begin.
		30		6.9	"	Vols. continue.
	52			6.8	"	"
		30		6.8	110	Vols. cease. Cover red.
	53			6.8	"	"
		30		6.8	"	"
Stopped	54			7.0	"	"

Cooled 3 minutes.

Coking - More coked than previously.

Percentage Volatiles

9.8336

9.4655

.3681

36.81%

SAMPLE No. 148, No. 5.

Crucible in Contact. Time 4 min.

	Time			Amperes.	Volts. Before 120	Heat and Volatils.
	Hr.	Min.	Sec.			
Start	10	51	0	8.3	115	
			15	7.3	"	
			30	7.2	"	
			45	7.0	"	
		52		7.0	"	Vols. begin.
			30	6.8	"	Vols. continue.
		53		6.7	"	"
			30	6.6	"	Vols. catch fire.
		54		6.6	"	Vols. cease
			30	6.5	"	No vols. Red cover.
Stopped		55		6.6	"	"

Cooled 3 minutes.
 Coking - Slightly coked.
 Percentage Volatils.
 9.8333
9.4671
 .3662

36.62%

SAMPLE No. 148, No. 6.

49

Wire Basket. Time 7 min.

	Time			Amperes.	Volts.	Heat and Volatiles
	Hr.	Min.	Sec.		Before 123.5	
Start	2	55	0	8.1	118	
			15	7.4	"	
			30	7.2	"	
			45	7.1	"	Red cover.
		56		6.8	116	Vols. begin
			30	6.8	"	Vols. continue
		57		6.8	"	"
			30	6.8	"	Vols. cease
		58		6.8	117	
		59		6.8	118	
		60		6.7	"	
		61		6.6	"	
Stopped		62		6.8	"	

Cooled 3 minutes.

Coked slightly.

Percentage Volatiles

9.8334

9.4656

.3678

36.78%

SAMPLE No. 148, No. 7.

	Wire Basket.			Time 7 min.		Heat and Volatiles
	Hr.	Min.	Sec.	Amperes.	Volts.	
Start	3	34	0	8.2	104	
			15	7.4	"	
			30	7.2	"	Red holes
			45	7.0	"	
	35			6.9	105	35.10 Vols begin.
			30	6.7	"	Vols. continue
	36			6.6	"	"
			30	6.5	"	Vols. cease.
	37			6.4	"	
	38			6.2	"	
	39			6.3	"	
	40			6.2	106	
Stopped	41			6.2	"	

Cooled 3 minutes.
 Coked slightly
 Percentage Volatiles
 9.8333
 9.4670

 .3663

36.63%

SAMPLE No. 148, No. 8.

51

Wire Basket. Time 7 minutes.

Start	Time			Amperes. Before 110	Volts.	Heat and Volatiles.
	Hr.	Min.	Sec.			
	4	35	0	7.8	---	
			5	7.6	105	
			10	7.4	"	
			15	6.8	"	
			30	6.8	"	
			45	6.7	"	
	36			6.5	"	Vols. begin.
		30		6.4	"	Vols. continue.
	37			6.3	"	Vols. catch fire
		30		6.2	"	Vols. cease
	38			6.2	"	
	39			6.5	105.5	Cover red
	40			6.8	118	Cover very bright red.
	41			6.9	"	"
Stopped	42			7.0	"	"

Cooled 3 minutes.

Coked slightly

Percentage Volatiles.

9.8335

9.4663

.3672

36.72%

SAMPLE No. 148, No. 9.

52

	Wire Basket.			Time 7 min.		Heat and Volatiles
	Hr.	Min.	Sec.	Amperes.	Volts.	
Start	5	34	0	8.2	Bef, 119 114	
			5	7.4	"	
			10	---	"	
			15	7.1	"	
			30	6.9	"	
			45	6.8	"	
	35			6.7	"	Vols. begin.
		30		6.6	"	Vols. continue.
	36			6.8	"	Vols. cease.
		30		6.8	"	Gases catch fire.
	37			6.6	"	Burning stops.
	38			6.6	"	
	39			6.8	113	
	40			6.6	"	
Stopped	41			6.6	"	

Cooled 3 minutes.

Coked slightly.

Percentage Volatiles:

9.8335

9.4665

36.70

36.70%

SAMPLE No. 148, No. 10.

Start	Wire Basket. Time			Time 7 min. Amperes. Volts.		Heat and Volatiles
	Hr.	Min.	Sec.	Before	118	
Start	10	15	0	8.8	113	
			5	7.6	"	
			10	7.3	"	
			15	6.7	"	
			30	6.6	"	
			45	6.6	"	
16				6.7	112	Vols. begin
			30	6.7	"	Vols. continue.
17				6.7	"	Vols. cease
			30	6.7	"	Gases catch fire } 15
18				6.7	"	Burning stops
19				6.7	"	
20				6.7	"	
21				6.6	"	
Stopped	22					

Cooled 3 minutes.

Coked slightly

Percentage Volatiles.

9.8332

9.4667

.3665

36.65%

SAMPLE I. No. 1.

54

	Time			Amperes.	Volts.	Volatiles
	Hr.	Min.	Sec.			
Start	10	15	0	7.8	114	
			15	6.9	"	
			30	6.7	"	
			45	6.5	"	
	16			6.4	"	Volts. begin.
			30	6.4	"	" continue
	17			6.4	"	Heavy vols.
			30	6.4	"	Volts. cease
	18			6.3	115	
			30	6.4	"	
Stopped	19			6.4	"	

Percentage Volatiles
 9.8323
9.3588
 .4735

47.35%

SAMPLE 1. No. 2.

55

	Time.			Amperes.	Volts.	Volatiles.
	Hr.	Min.	Sec.		Bef. 124	
Start	11	24	0	8.2	118	
			15	7.1	"	
			30	6.8	"	
			45	6.6	"	
	25			6.4	"	Vols. begin.
		30		6.3	117	Vols. continue.
	26			6.2	"	"
		30		6.2	116	Vols. cease
	27			6.1	"	
		30		6.1	"	
Stopped	28			6.1	"	

Percentage Volatiles
 9.8322
9.3591
 .4731

47.31%

Sample I. No. 3.

	Time			Amperes.	Volts.	Volatiles.
	Hr.	Min.	Sec.		Bef. 116	
Start	2	20	0	7.9	111	
			15	7.0	"	
			30	6.9	"	
			45	6.8	"	
	21			6.6	"	Vols. begin
		30		6.7	"	Vols. continue
	22			6.7	110	Vols. cease
		30		6.7	109	
	23			6.7	"	
		30		6.7	"	
Stopped	24			6.8	"	

Percentage Volatiles.
 9.8321
9.3578
 .4743

47.43%

SAMPLE I. No. 4.

	Time.			Amperes.	Volts. Bef. 124	Volatiles.
	Hr.	Min.	Sec.			
Start	3	45	0	7.8,	119	
			15	6.7	"	
			30	6.5	"	
			45	6.3	"	
	46			6.2	"	Vols. begin.
		30		6.1	"	Vols. continue.
	47			6.1	"	Vols. catch fire.
		30		6.1	"	Vols. cease.
	48			6.1	"	
		30		6.2	120	
Stopped	49			6.3	121	

Percentage Volatiles.
 9.8323
 9.3587
 —————
 .4736

47.36%

SAMPLE I. No. 5.

	Time			Amperes.	Volts. Bef. 118	Volatiles
	Hr.	Min.	Sec.			
Start	10	30	0	8.0	114	
			15	7.2	"	
			30	6.8	"	
			45	6.7	"	
	31			6.6	"	Vols. begin.
		30		6.6	115	Vols. continue.
	32			6.6	"	Vols. cease
		30		6.6	"	
	33			6.5	"	
		30		6.4	116	
Stopped	34			6.3	"	

Percentage Volatiles.
 9.8322
9.3588
 .4734

47.34%

SAMPLE I. No. 6.

Time.			Amperes.	Volts.	Volatiles.
Hr.	Min.	Sec.		Bef. 119	
start	2	18	0	8.2	113
			15	7.1	"
			30	6.8	"
			45	6.8	" Vols. begin.
	19			6.6	" Vols. continue.
			30	6.5	"
	20			6.4	" 45 Vols. cease
			30	6.5	"
	21			6.5	"
			30	6.5	"
Stopped	22			6.5	"

Percentage Volatiles.
 9.8324
9.3579
 .4745

47.45%

SAMPLE I. No. 7.

	Time.			Amperes.	Volts. Bef. 114	Volatiles.
	Hr.	Min.	Sec.			
Start	5	10	0	8.5	109	
			15	7.3	"	
			30	7.2	"	
			45	7.1	"	
	11			7.0	108	Volts. begin
			30	7.1	"	" continu.
	12			6.9	109	" "
			30	6.9	108	" cease
	13			6.9	"	Gases catch
			30	7.0	"	fire.
Stopped	14			7.2		

Percentage Volatiles.

9.8324

9.3595

.4729

47.29%

SAMPLE I. No. 8.

	Time.			Amperes.	Volts.	Volatiles
	Hr.	Min.	Sec.		Bef. 113	
Start	9	42	0	8.1	108	
			15	7.3	"	
			30	7.0	"	
			45	6.9	"	
	43			6.8	"	Vols. begin.
		30		6.7	"	Vols. continue,
	44			6.7	"	"
		30		6.7	"	Vols. cease
	45			6.7	107	Gases catch fire.
		30		6.7	"	
Stopped.	46			6.6	"	

Percentage Volatiles.

9.8322

9.3588

.4734

47.34%

SAMPLE I. No. 9.

	Time.			Amperes.	Volts. Bef. 121	Volatiles
	Hr.	Min.	Sec.			
Start 1	45	0		7.7	117	
		15		6.8	"	
		30		6.7	"	
		45		6.6	"	
	46			6.4	"	Volts. begin.
		30		6.3	"	Volts continue.
	47			6.3	"	Volts cease.
		30		6.3	"	
	48			6.3	"	
		30		6.4	"	
Stopped	49			6.4	"	

Percentage Volatiles
 9.8322
9.3584
 .4738

47.38%

SAMPLE I. No. 10.

Start.	Time			Amperes.	Volts.		Volatiles.
	Hr.	Min.	Sec.		Bef.	121	
	4	12	0	8.4		115	
			15	7.2		"	
			30	6.9		"	
			45	6.7		"	
		13		6.7		116	Vols. begin.
			30	6.6		114	Vols. continue.
		14	30	6.6		115	"
			30	6.6		114	Vols. cease
		15		6.5		"	
			30	6.4			
Stopped		16		6.5			

Percentage Volatiles.
 9.8323
9.3579
 .4744

47.44%