

The Composition
of the
ELECTRODE DEPOSIT
in the
MOORE LAMP.

T.P. HASLAM CLASS OF 1908.

BIBLIOGRAPHY:

Vol. xxvi N° 4, the April number of the proceedings of the American Institute of Electrical Engineers.

Vol. 4, 1871, Berichte der Deutschen Chem. Gesellschaft, page 497.

The Moore Lamp consists essentially of a piece of glass tubing one and three-fourths inch in diameter and four or more feet in length, into both ends of which are sealed carbon electrodes. The tube contains a gas under a pressure of about .1 m. m. of mercury.

If the tube is filled with carbon dioxide an intense white light is given and if nitrogen is used the light has a yellowish cast.

When an otherwise properly constructed lamp is sealed up, without being connected to a pressure regulator, after the passage of the current for a few minutes the pressure becomes so much reduced that the light first begins to flicker, then goes out.

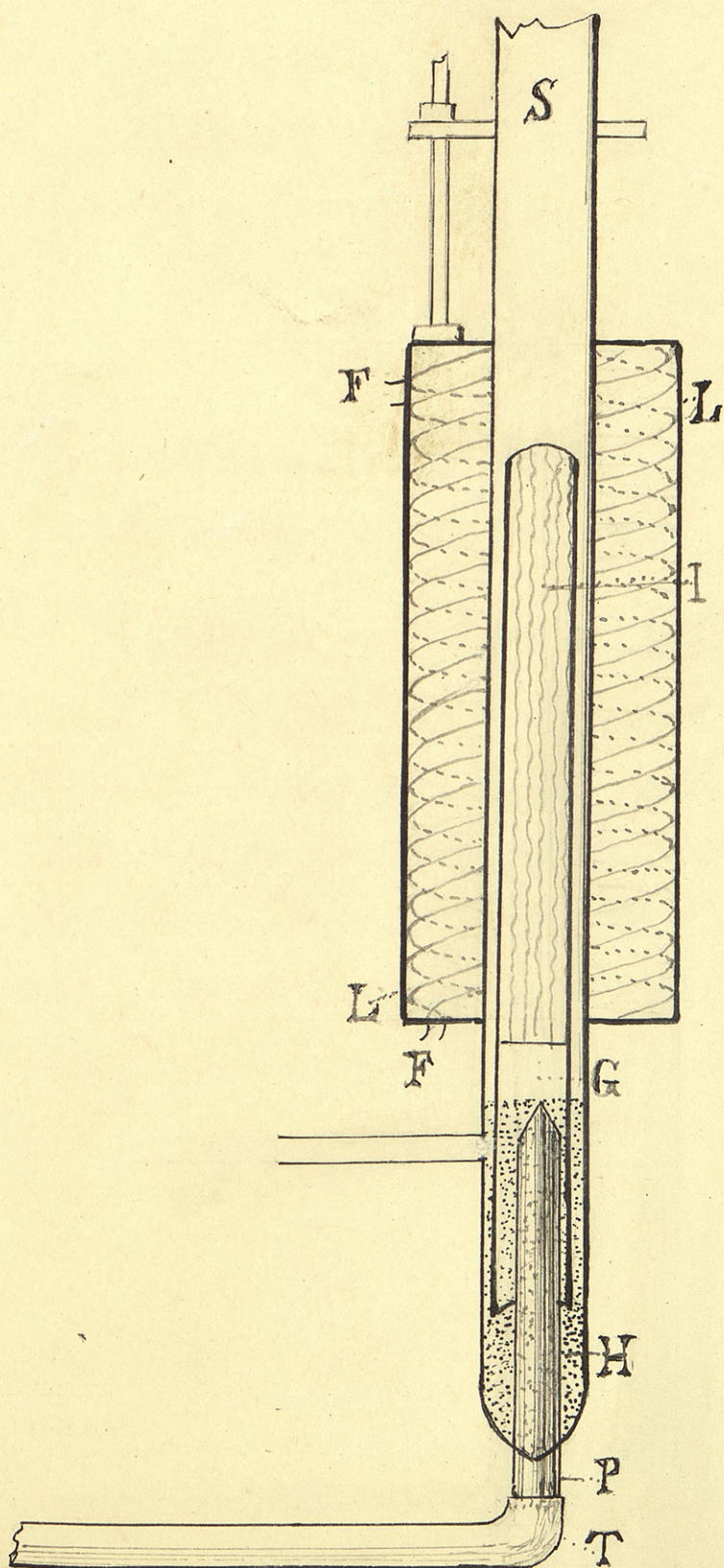
In order to prevent this, Mr. Moore has invented an automatic device for admitting more of the gas. It is constructed as follows: -

P is a carbon pencil cemented into the

neck of the tube **S**, at the origin of **T**. The carbon pencil is immersed in a bath of mercury ^{**H**} into which dips the end of a glass tube **G**, the upper part of which is filled with iron wire ^{**I**}. Around the upper part of the outside of the tube **S** is a solenoid of iron, (shown in cross section at **LL**), which is in series with the low-tension side of the transformer used to obtain the necessary voltage. The tube **S** leads to the supply of gas, and the tube **T** to the vacuum tube.

Now, when the pressure becomes too low in the tube, the current in the solenoid, since it is in series with the transformer, is increased. This action raises the iron wire and the tube **G** and allows the mercury to fall till its surface is below the tip of the carbon pencil. The carbon is not porous to the mercury, but is to the gas, and so a little gas is allowed to pass through. This reduces the current in the solenoid, the action is reversed and the supply of gas cut off.

The nitrogen is obtained from the air by passing it over phosphorus, and the carbon dioxide is obtained from hydrochloric acid and marble.



Fitted in this way a lamp will run for two years, or perhaps more, without attention. During this time in the neighborhood of the electrodes, a considerable quantity of a deposit accumulates.

The composition of this deposit is the subject of this

Thesis.

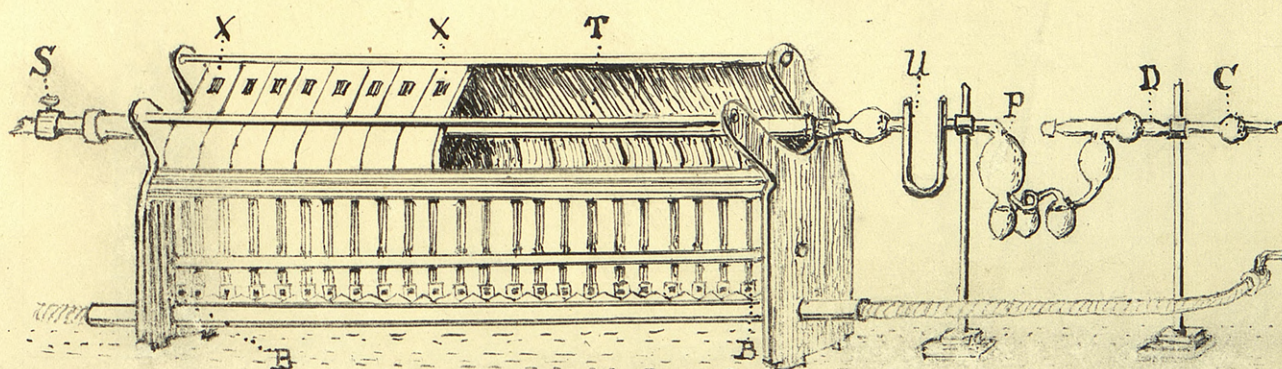
The methods used for the determination of nitrogen, carbon and hydrogen were taken directly from Gatterman's Practical methods of Organic Chemistry (Pages 85 to 111)

They were, in brief, as follows:—

For the determination of nitrogen a Jena combination tube about 10 c.m. longer than the furnace was selected and fitted as the accompanying diagram will show

Combustion Furnace.
with
 Absorption Apparatus for the Determination of
CARBON and HYDROGEN.

S	Glass Stopcock
X	Tiles
T	Combustion Tubes
B	Burners
U	U-Tubes
P	Potash Bulbs
D	Drying Tube
C	Chloride Tube





5 cm free.

10 cm reduced copper spiral,

35 cm coarse copper oxide.

10 cm fine copper oxide mixed with the substance.

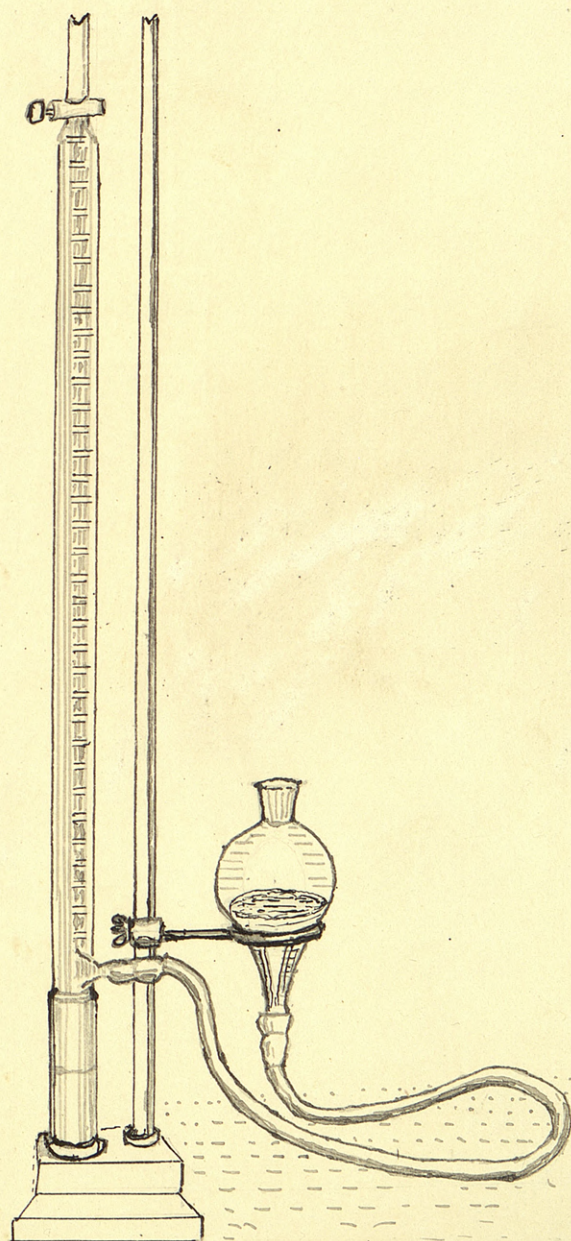
15 cm coarse oxide.

3 cm copper spiral.

5 cm free.

The supply of carbon dioxide was obtained from sodium hydrogen carbonate. A soft glass tube closed at one end was filled three-fourths full of this substance and gently heated in another combustion furnace. A small U tube containing a little sulphuric acid was interposed between the generator and the rear of the combustion furnace.

The nitrogen was collected in an azotometer the essentials of which the following diagram will serve to make clear.



The combustion is begun by lowering the reservoir of the azotometer and passing a rapid current of carbon dioxide through the tube for about fifteen minutes. The reservoir is then raised, the stop cock closed, and if, after two minutes, only a minimum quantity of fine foam collects in the top of the azotometer the conclusion is that the air in the combustion tube is displaced by carbon dioxide.

The combustion is then continued by gradually bringing the whole tube to a dull redness, and, after the last portion of the tube is at this temperature the nitrogen, which then largely fills the tube, is replaced by carbon dioxide as at the beginning of the experiment.

Before the copper oxide is used it is strongly heated in the air, in a copper dish made by turning up the edges of a piece of heavy sheet copper.

The copper spiral is reduced by heating to redness and plunging it into a test tube containing 2 cc. of C.P. methyl alcohol.

For the determination of carbon the tube was filled as shown in the following diagram.



5 cm free.

short copper spiral.

45 cm coarse oxide.

short copper spiral.

12 cm free.

15 cm copper oxide spiral.

15 cm free.

The tube thus filled was placed in the furnace and heated to redness through the entire length, while a current of oxygen which had been purified by passing successively through soda lime, calcium chloride and con. sulphuric acid, was passed through (In the burning of the nitrogenous substance a current of air was used.) After the tube was heated to a dull redness the front end was protected by a calcium chloride tube and the burners under the rear end extinguished. When the rear end was sufficiently cooled the stopper bearing the glass stop cock was removed, the copper oxide spiral taken out and a copper boat filled with .1 to .4 gram of the substance intimately mixed with fine copper oxide, pushed carefully into the tube, the copper oxide spiral and the stopper with the glass stop cock replaced.

The substance was then burned ^{much} as in the determination of nitrogen, except ^{that} in the case of the non nitrogenous substance a slow current of oxygen was passed through the tube until at the close of the determination it inflamed a glowing splinter held at the end of the potash bulb. In the case of the ~~xxx~~ nitrogenous substance, the oxygen was not passed in until near the close of

the determination

The gases evolved during the experiment were passed first through a U tube filled with calcium chloride to absorb the water formed and then through a potash bulb containing a concentrated solution of caustic potash, in order to absorb the carbon dioxide formed.

Early in the experiment it was observed that the U tubes and potash bulbs would, upon standing either in the air or in the desiccator undergo a change, amounting sometimes to three or four milligrams. On this account it was decided to overcome this source of error before running the others.

The first method tried was that of moistening the tube, then wiping it off with a dry cloth, thus weighing with the maximum amount of water the tubes would hold on their surfaces.

The following tables will show in each case First: - The amount which any weighing differs from the first weight of the tube taken, and

Second: - The amount by which any two succeeding weights differ from each other, together with such other data as will serve to make the reason for the discrepancy clear.

The following table shows the variation when

one U tube with bulb in one side tube is used, fitted with rubber stoppers and caps made of very heavy seamless tubing and short pieces of a glass rod.

	I	II	III	IV	V	VI	VII	VIII
Time since previous weighing	5 min.	5 min.	5 min.	2 hrs	5 min.	5 min.	5 min.	5 min.
First weight	69.2581	69.2581	69.2581	69.2581	69.2581	69.2581	69.2581	69.2581
Successive weights	69.2553	69.2553	69.2553	69.2567	69.2560	69.2572	69.2559	69.2504
Difference from first weight	-28	-28	-28	-14	-21	-9	-22	-77
First weight	69.2581	69.2553	69.2553	69.2553	69.2567	69.2560	69.2572	69.2559
Second weight	69.2553	69.2553	69.2553	69.2567	69.2560	69.2572	69.2559	69.2504
Difference between consecutive weights	-28	0000	0000	+14	-7	+12	-13	-55
Treatment.	moistened and wiped	moistened and wiped	moistened and wiped	moistened and wiped	moistened and wiped	moistened and wiped	moistened and wiped	moistened and wiped

This method was then discarded and the chloride tube was placed in a large desiccator over calcium chloride. The balance was dried with a beaker of concentrated sulphuric acid.

The following table shows the results.

	I	II	III	IV
Time between weighings	5 min.	1 hr.	5 min.	3 hrs.
First weight	69.2565	69.2565	69.2565	69.2565
Successive weights	69.2565	69.2571	69.2571	69.2518
Difference from first weight	0000	+6	+6	-47
First weight.	69.2565	69.2565	69.2571	69.2571
Second weight.	69.2565	69.2571	69.2571	69.2518
Difference between consecutive weights	0000	+6	0000	-53

It will be observed that a steady loss in weight on standing occurred. A second U tube was then fitted similar to the first. The appended table shows the difference in weight

between the two tubes.

Time between weighings	I 5 min.	II 30 min.	III 35 min.	IV 1 hr 50 min.	V 15 hrs. 10 min.	VI 5 min.	VII 5 min.	VIII 5 min.
First weight	5.8006	5.8006	5.8006	5.8006	5.8006	5.8006	5.8006	5.8006
Successive weights	5.8009	5.8009	5.8007	5.8007	5.8008	5.8011	5.8036	5.8039
Difference from first weight	+3	+3	+1	+1	+12	+5	+30	+33
First weight	5.8006	5.8009	5.8009	5.8007	5.8007	5.8018	5.8011	5.8036
Second weight	5.8009	5.8009	5.8007	5.8007	5.8018	5.8011	5.8036	5.8039
Difference between consecutive weights.	+3	0000	-2	0000	+11	-7	+25	+3
Remarks.	stood in air. Caps not removed.	stood in air. Caps not removed.	stood in air. Caps not removed.	stood in air. Caps not removed.	stood over night in air. Caps not removed.	stood in air. Caps removed and brushed.	stood in air. Caps removed and brushed.	stood in air. Caps removed and brushed.

Note that a considerable increase in weight occurs upon standing over night, and that this was partially corrected by removing the caps and then replacing them.

Thinking that, perhaps, the difficulty in obtaining concordant weighings was due, in part, to the rubber caps and stoppers of the U tubes, tubes were selected having ground glass stoppers. Two of these were filled and the variations recorded as before.

	I	II	III	IV	V
Time between weighings.	4 hrs. 15 min.	5 min.	13 hrs.	5 min.	6 hrs.
First weight	3.7040	3.7040	3.7040	3.7040	3.7040
Successive weights	3.7042	3.7042	3.7033	3.7034	3.7035
Difference from first weight	+0.0002	+0.0002	-0.0007	-0.0006	-0.0005
First weight.	3.7040	3.7042	3.7042	3.7033	3.7034
Second weight.	3.7042	3.7042	3.7033	3.7034	3.7035
Difference between successive weights	+0.0002	0000	-0.0009	+0.0001	+0.0001
Remarks.	cock not opened. stood in air.	Cock opened. stood in air.	cock opened. stood in air over night.	Both tubes wiped with a dry cloth.	Cock opened. stood in air.

A somewhat similar investigation was carried on with respect to the Potash Bulbs.

Potash bulb moistened and wiped with a dry cloth:-

	I	II	III	IV
Time between weighings.	5 min.	5 min	5 min	30 min.
First weight	54.4314	54.4314	54.4314	54.4314
Successive weights	54.4310	54.4307	54.4312	54.4329
Difference from first weight.	-.0004	-.0007	+0002	+0015
First weight	54.4314	54.4310	54.4307	54.4316
Second weight	54.4310	54.4307	54.4316	54.4329
Difference between consecutive weights.	-.0004	-.0003	+0009	+0013
Remarks.	Moistened and wiped.	Moistened and wiped.	Moistened and wiped.	Moistened and wiped. Then stood in air 30 minutes.

Variation in weight of two similar potash bulbs.

	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
Time between weighings.	4 hrs. 30 min.	5 min.	1 hr.	15 min.	45 min.	5 min.	10 hrs.	5 min.	2 hr.	15 min.	4 hrs. 20 min.	
First weight.	7.7280	7.7280	7.7280	7.7280	7.7280	7.7280	7.7280	7.7280	7.7280	7.7280	7.7280	7.7280
Successive weights.	7.7274	7.7283	7.7283	7.7275	7.7275	7.7275	7.7258	7.7260	7.7265	7.7265	7.7265	7.7265
Difference from first weight.	-.0006	+0003	+0003	-.0005	-.0005	-.0005	-.0022	-.0020	-.0015	-.0015	-.0015	-.0015
First weight.	7.7280	7.7274	7.7283	7.7283	7.7275	7.7275	7.7275	7.7258	7.7260	7.7265	7.7265	7.7265
Second weight.	7.7274	7.7283	7.7283	7.7275	7.7275	7.7275	7.7258	7.7260	7.7265	7.7265	7.7265	7.7265
Difference between consecutive weights.	-.0006	+0009	0000	-.0008	0000	0000	-.0017	+0002	+0005	-.0002	+0007	
Remarks.	wiped with dry cloth. stood in air.	stopper opened	stood in air.	wiped with dry cloth. stood in air.	stood in air.	Rubber brushed	stood in air over night.	stopper opened.	stood in air.	wiped with dry cloth.	stood in air.	

The U tubes and potash bulbs were then immersed in a beaker containing a solution of $K_2Cr_2O_7$ in concentrated H_2SO_4 .

Variation in weight of the two glass stoppered U tubes.

	I	II	III
Time between weighings.	6 hrs. -	4 hrs.	24 hrs., 15 min.
First weight.	3.7892	3.7892	3.7892
Successive weights.	3.7892	3.7892	3.7892
Difference from first weight.	0000	0000	0000
First weight.	3.7892	3.7893	3.7892
Second weight.	3.7892	3.7892	3.7892
Difference between consecutive weights.	0000	-0001	0000
Remarks.	Stop cock opened - stood in air.	Stop cock opened - stood in air.	Stop cock opened - stood in air.

Note that this is the first case in which a very considerable change has not resulted from the tubes standing over night. During the subsequent analyses the weight of U tubes was frequently checked and after periods of from twelve to fifty-six hours the weight had not changed.

Variation in weight of the two potash bulbs.

	I	II	III	IV	V	VI
Time between weighings	5 min.	5 min.	5 min.	5 hrs	5 hrs. 30 min.	14 hrs. 30 min.
First weight.	2.1341	2.1341	2.1341	2.1341	2.1341	2.1341
Successive weights.	2.1341	2.1339	2.1341	2.1341	2.1336	2.1337
Difference from first weight.	0000	-0002	0000	0000	-0005	-0004
First weight.	2.1341	2.1341	2.1339	2.1341	2.1341	2.1336
Second weight.	2.1341	2.1339	2.1341	2.1341	2.1336	2.1337
Difference between consecutive weights.	0000	-0002	+0002	0000	-0005	+0001
Remarks.	Brushed in air	Cap removed from tube and replaced	Cap removed from both and replaced	In air in weighing room.	One stopper leaked - (was too loose)	In air in weighing room - (opened to air.)

These results were considered as good as could be ex-

pected and all subsequent weighings of the K.OH bulbs made by this method. The cleaning mixture probably removes hygroscopic mineral substances from the outside of the tubes, as well as freeing them from organic matter.

In the first two determinations of nitrogen a Kipp generator, charged with marble and dilute hydrochloric acid, was used to supply the carbon dioxide. After the determinations were finished it was found upon testing the purity of the carbon dioxide that it contained a small residue of some gas which was not absorbed by the potash solution in the azotometer. This was probably due to the gas occluded by the marble.

The percentage composition of the deposit formed when nitrogen is used in the lamp is shown in the following table.

Determination No.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
I	* 34.05	* 3.6	17.55	44.8
II	35.9	3.4	16.4	44.3
III	35.07	3.4	17.33	44.3
IV	35.1	3.4	17.33	

* A different sample.

Dividing the percentage compositions by the atomic weight of each element we get for the empirical formula either $C_3H_3ON_3$ or $C_6H_7ON_6$, if we consider

hydrogen $3\frac{1}{2}$, then multiply by two.

In Richters Index the formula, $C_3H_3ON_3$ is assigned to azulminic acid.

The properties of the substance analyzed agree with those of azulminic acid as described by Jacobson and Emmerling.

It is a brownish black solid, difficultly soluble in water, somewhat soluble in ammonium hydroxide, very soluble in concentrated sulphuric acid; the solution having a green fluorescence. It is soluble in nitric acid. sp. gr. 1.4, the solution being dark brown. Upon heating for a short time on the water bath, the solution changes to a reddish yellow, and upon cooling, if the solution was quite concentrated, reddish yellow crystals are deposited. These crystals are very minute, and under the microscope have the appearance of small beads arranged in strings.

The solution of this precipitate in concentrated H_2SO_4 exhibits a greenish fluorescence.

A small quantity of azulminic acid was synthesized by passing cyanogen into concentrated ammonium hydroxide. The azulminic acid separating out in dark brown flakes was

filtered off. The properties of the azulminic acid thus prepared agreed exactly with those of the deposit, except that the synthetic product exhibited fluorescence to a much greater extent.

An analysis of the deposit formed when
Carbon Dioxide
is used in the lamp was made.
The following table shows the composition.

Determination No.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
I	54.4	3.57	42.03	.114
II	54.6	2.99	42.41	.110
III	54.6	3.24	42.16	

Dividing the percentage composition by the atomic weight, we get for the empirical formula $C_{4.5} H_3 O_{2.6}$, or, $C_9 H_6 O_5$

The following table shows the substances having this formula, together with their melting points, as given in Richters Index:—

- | | |
|---|------------|
| 1 Opinsäure | Sm 1448 |
| 2 Benzol-1-Carbonsäure-2-Ketocarbonsäure + 2H ₂ O | Sm 144.3° |
| 3 3-4-Dioxybenzol methyleneäther-1-Ketocarbonsäure | Sm 148-149 |
| 4 Anhydred-d-3-4-Dioxybenzol-4-methyläther 1, 2-dicarbonsäure | Sm 148 |
| 5 -2-Aldehyd-d-Benzol-1-2-3, Tricarbonsäure | Sm 149 |

As the substance under investigation does not melt below a red heat, it would not seem to be any of the above named substances. Want of time has prohibited further investigation.