rous acid (for $\overset{-}{HO} + \overset{+}{Cl}$) may be, it involves the *fact* of the existence of *positive chlorine ions.*

It must be added that these views would have been published long ere this, if it had not been the hope of the author to report at the same time on other direct experimental confirmations of them. Circumstances have made it impossible to undertake before this the delicate work involved; but in the ensuing year it is intended at least to study the behavior, of solutions of chlorine, hypochlorous acid, iodine chloride, etc., towards the electric current, in the hope of proving that, under suitable conditions, the migration of positive halogen ions to the negative pole will take place. Such a migration would decide the question, it seems to me, in the most direct and unquestionable fashion. I regret that the interesting paper of Professor Noyes and Mr. Lyons has made it necessary to publish these lines rather prematurely; but their invitation for discussion encourages me to do so before the completion of my own experiments.

UNIVERSITY OF CHICAGO,
August 3, 1901.

THE PHOTOMETRIC DETERMINATION OF SULPHATES.

BY D. D. JACKSON.

Received September 3, 1901.

THE time element enters largely into most transactions in the industrial world and chemistry as a pure science is not always to be considered. Exact methods, if time-consuming, must give place, in many cases, to rapid tests that give practical knowledge in the shortest possible limit of time.

If a trainload of coal is detained for inspection it is not feasible to wait a day or two for an ultimate analysis by organic combustion. The heating power is obtained in an hour and a half by calorimetry. By this same process, using the Mahler bomb, the determination of volatile sulphur, which would take two hours by ordinary chemical methods, may be accomplished by photometry in five minutes,—not with great accuracy, but with sufficient accuracy for practical purposes.

The physician in analyzing urine does not desire to know the exact percentage of sulphates present, but merely to what extent the amount present is below or above the normal. Photometry tells him this in a few minutes.

The determination of sulphates as an adulterant in cement where large constructional works are being carried out may necessitate the analysis of some twenty-five samples of cement daily. This is impractical, if not impossible, by ordinary methods; but by photometry it may be easily accomplished. A limiting figure is placed upon the amount of sulphates present in the cement by the specifications of the contract and, unless the figure found is very close to that of the specifications, the photometric process is quite accurate enough. Nearly all of the determinations may be disposed of in this manner, while the questionable ones may be determined, if necessary, by more accurate gravimetric methods. In this way a needless expense of time and energy is avoided. Many other instances might be cited where the photometric determination of sulphates would be highly practical.

Professor Hinds[1] was the first to suggest the photometric analysis of precipitates, and a year ago[2] he published tables to facilitate this process. Since that time the author has had occasion to use this method quite extensively in the determination of sulphur and sulphuric acid, and has made at the same time a large number of gravimetric determinations to check the results. Experiments have also been made with known solutions of sulphates and with sulphuric acid. It has been found in this manner that certain modifications of Professor Hinds' method greatly increase the ease and accuracy with which these determinations may be made.

It was noted that differences in the brightness of the candle employed and differences in the distance of the candle from the bottom of the tube, as well as of the eye of the observer from the top of the tube, made appreciable differences in the results. Accordingly, a series of experiments was made to determine the process whereby the most accurate figures might be obtained. The readings in many cases were made by four different observers, so that the personal element would be eliminated. Experiments were also made with the diaphenometer of Hornung,[3] modified by Parmelee and Ellms;[4] but, while this works very well in the determination of the turbidity in water, it was not found to be as convenient or as accurate for the determination of sulphates as the

---

[1] This Journal, **18**, 661.

[2] *Ibid.*, **22**, 269.

[3] *Eng. News*, April 2, 1896.

[4] *Tech. Quart.*, **12**, No. 2, June, 1899.

photometer of Hinds. The details of the method finally decided upon are as follows :

A very simple piece of apparatus is employed. It consists of a 100 cc. Nessler jar, 2.5 cm. in diameter, and 17 cm. to the 100 cc. mark. The dimensions need not be exact, but this is the size which is found to be most convenient. This jar is graduated from the bottom up in centimeters and millimeters to avoid constantly measuring the depth with a rule.

A standard candle is used, having just one candle power. Above this is suspended an iron ring with an indicator so that the top of the ring is always just three inches above the top of the candle itself. This brings the top of the flame in close proximity to the bottom of the tube, but just far away enough to prevent smoking or excessive heating.

The observations are made in a dark room and the candle is placed over a dark surface. The tube which is to contain the solution is enveloped in a brass holder which comes up almost to the 100 cc. mark and has a broad disk at the bottom which shields the eye from the strong light below. The bottom of this cylindrical shaped tube is entirely open except for a very narrow rim which serves to keep the glass tube in place. The inside of the holder is painted a dull black to prevent reflection.

The solution to be determined for sulphates is washed into the 100 cc. Nessler jar and made slightly acid with hydrochloric acid. Distilled water at room temperature is then added nearly to the 100 cc. mark. About 2 grams of pure solid barium chloride are added, and the solution made up exactly to the 100 cc. mark. A pure rubber stopper is placed in the top of the tube and the whole shaken thoroughly until the barium chloride is dissolved.

In a few minutes the solution is ready to be examined. The tube is placed in the brass holder and its contents are poured back and forth from the glass tube into a lipped beaker, keeping the precipitate constantly shaken up, so that throughout the liquid the turbidity is uniform.

When the holder containing the tube is placed on an iron ring suspended three inches above the top of the candle and the eye is held quite near the top of the glass tube, a point is finally reached where the flame of the candle just disappears. The height to which the solution stands in the tube (reading the bottom of the meniscus) is then taken and from this reading the per cent. of sulphates may be calculated from the formula

$$x = \frac{0.0574}{y + 0.1},$$

where x equals grams of sulphur trioxide required, and y equals the depth in centimeters of the liquid in the cylinder.

This calculation is avoided and thereby considerable time saved by the use of the following table:

TABLE FOR THE PHOTOMETRIC DETERMINATION OF SULPHURIC ACID.

cm.	SO_3. Gram.	cm.	SO_3. Gram.	cm.	SO_3. Gram.	cm.	SO_3. Gram.
1.0	0.0522	4.0	0.0140	7.0	0.0081	10.0	0.0057
1.1	0.0478	4.1	0.0137	7.1	0.0080	10.2	0.0056
1.2	0.0442	4.2	0.0133	7.2	0.0079	10.4	0.0055
1.3	0.0410	4.3	0.0131	7.3	0.0078	10.6	0.0054
1.4	0.0383	4.4	0.0128	7.4	0.0077	10.8	0.0053
1.5	0.0359	4.5	0.0125	7.5	0.0076	11.0	0.0052
1.6	0.0338	4.6	0.0122	7.6	0.0075	11.2	0.0051
1.7	0.0319	4.7	0.0119	7.7	0.0074	11.4	0.0050
1.8	0.0302	4.8	0.0117	7.8	0.0073	11.6	0.0049
1.9	0.0287	4.9	0.0115	7.9	0.0072	11.8	0.0048
2.0	0.0273	5.0	0.0113	8.0	0.0071	12.0	0.0047
2.1	0.0261	5.1	0.0110	8.1	0.0070	12.2	0.0047
2.2	0.0250	5.2	0.0108	8.2	0.0069	12.4	0.0046
2.3	0.0239	5.3	0.0106	8.3	0.0068	12.6	0.0045
2.4	0.0230	5.4	0.0104	8.4	0.0068	12.8	0.0044
2.5	0.0221	5.5	0.0103	8.5	0.0067	13.0	0.0044
2.6	0.0213	5.6	0.0101	8.6	0.0066	13.5	0.0042
2.7	0.0205	5.7	0.0099	8.7	0.0065	14.0	0.0041
2.8	0.0198	5.8	0.0097	8.8	0.0064	14.5	0.0039
2.9	0.0191	5.9	0.0096	8.9	0.0064	15.0	0.0038
3.0	0.0185	6.0	0.0094	9.0	0.0063	15.5	0.0037
3.1	0.0179	6.1	0.0093	9.1	0.0062	16.0	0.0036
3.2	0.0173	6.2	0.0091	9.2	0.0062	16.5	0.0035
3.3	0.0168	6.3	0.0090	9.3	0.0061	17.0	0.0034
3.4	0.0164	6.4	0.0088	9.4	0.0060	17.5	0.0033
3.5	0.0159	6.5	0.0087	9.5	0.0060	18.0	0.0032
3.6	0.0155	6.6	0.0086	9.6	0.0059	18.5	0.0031
3.7	0.0151	6.7	0.0084	9.7	0.0059	19.0	0.0030
3.8	0.0147	6.8	0.0083	9.8	0.0058	19.5	0.0029
3.9	0.0144	6.9	0.0082	9.9	0.0057	20.0	0.0029

SULPHATE IN CEMENT.

Treat 1 gram of cement with strong hydrochloric acid, add water and evaporate to dryness. Add a small amount of concentrated hydrochloric acid, then add an equal amount of boiling water and filter into a 100 cc. graduated tube, make up to the mark with cold water, and proceed with the photometric method as directed.

If exactly 1 gram is taken, and the reading on the tube is 4.3 cm., then from the table, 1 gram contains 0.0131 gram of sulphur trioxide, or 1.3 per cent. sulphur trioxide.

Specifications usually state that not over 1.5 per cent. sulphur trioxide can be accepted. 2 per cent. is sometimes used as a limiting figure.

SULPHATE IN URINE.

Filter the urine, if turbid, and take 10 cc., make it slightly acid with hydrochloric acid and add water nearly to the 100 cc. mark. Add about 2 grams of solid barium chloride, make up to the 100 cc. mark, and proceed as directed in the method.

If 10 cc. are taken and the reading on the tube is 4.6, then from the table, 10 cc. equals 0.0122 gram sulphur trioxide, or 0.12 per cent.

Normal urine varies from 0.10 to 0.15 per cent. sulphur trioxide.

SULPHATE IN WATER.

100 cc. may be taken for well waters, but some well waters and many surface waters will need to be concentrated in order to get accurate results.

A quick determination in waters low in sulphates may be roughly made by taking 100 cc. of water, acidifying slightly with hydrochloric acid and adding solid barium chloride. After shaking well, the turbidity is compared with silica standards sidewise toward the light. These silica standards have been used in the determination of the turbidity of drinking water.[1]

A standard of ten in silica is equivalent to a turbidity produced by 1.45 parts per million of sulphur trioxide. The photometric method, while not as rapid as this for solutions requiring concentration, is, however, much more accurate. The reason for this will be shown by a study of the diagram given later, in which it is seen that the results do not follow the reciprocal curve.

SULPHATE IN COAL.

After fusion by the ordinary method, the sulphate in coal may

---

[1] **Whipple, G. C.**, and **Jackson, D.D.**: *Tech. Quart.*, **12**, No. 4, Dec. 1899; **13**, No. 3, Sept., 1900.

be determined photometrically; but when the Mahler bomb is used, the volatile sulphur is all in solution in the water at the bottom of the bomb. This water is filtered and titrated with 0.1 normal sodium carbonate, using methyl orange as an indicator to get the nitric acid present. It is then ready for the determination of sulphur by photometry. The pink color of the solution does not interfere with the results.

The following is a special table calculated for the determination of sulphur:

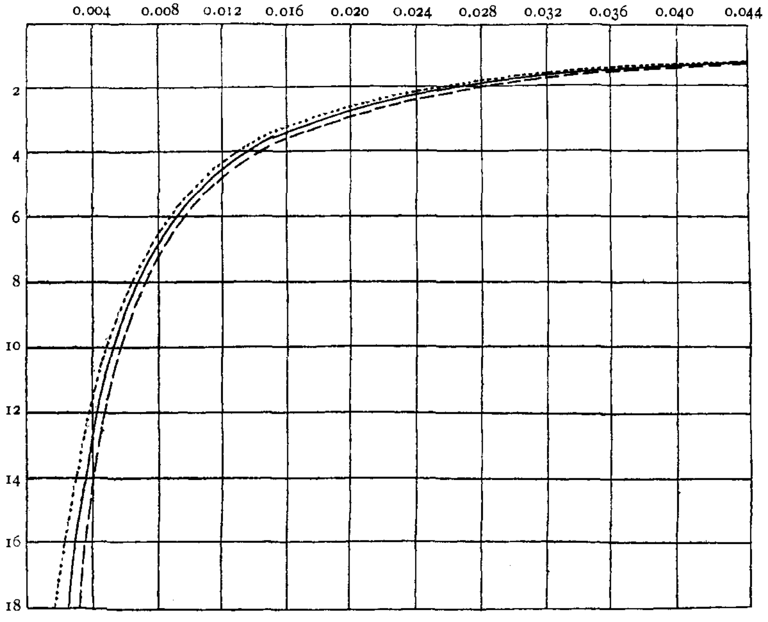
Table for the Photometric Determination of Sulphur.

cm.	Sulphur. Gram.	cm.	Sulphur. Gram.	cm.	Sulphur. Gram.	cm.	Sulphur. Gram.
1.0	0.0209	4.0	0.0056	7.0	0.0032	10.0	0.0023
1.1	0.0191	4.1	0.0055	7.1	0.0032	10.2	0.0022
1.2	0.0177	4.2	0.0053	7.2	0.0032	10.4	0.0022
1.3	0.0164	4.3	0.0052	7.3	0.0031	10.6	0.0022
1.4	0.0153	4.4	0.0051	7.4	0.0031	10.8	0.0021
1.5	0.0144	4.5	0.0050	7.5	0.0030	11.0	0.0021
1.6	0.0135	4.6	0.0049	7.6	0.0030	11.2	0.0020
1.7	0.0128	4.7	0.0048	7.7	0.0030	11.4	0.0020
1.8	0.0121	4.8	0.0047	7.8	0.0029	11.6	0.0020
1.9	0.0115	4.9	0.0046	7.9	0.0029	11.8	0.0019
2.0	0.0109	5.0	0.0045	8.0	0.0028	12.0	0.0019
2.1	0.0104	5.1	0.0044	8.1	0.0028	12.2	0.0019
2.2	0.0100	5.2	0.0043	8.2	0.0028	12.4	0.0018
2.3	0.0096	5.3	0.0042	8.3	0.0027	12.6	0.0018
2.4	0.0092	5.4	0.0042	8.4	0.0027	12.8	0.0018
2.5	0.0088	5.5	0.0041	8.5	0.0027	13.0	0.0018
2.6	0.0085	5.6	0.0040	8.6	0.0026	13.5	0.0017
2.7	0.0082	5.7	0.0040	8.7	0.0026	14.0	0.0016
2.8	0.0079	5.8	0.0039	8.8	0.0026	14.5	0.0016
2.9	0.0076	5.9	0.0038	8.9	0.0026	15.0	0.0015
3.0	0.0074	6.0	0.0038	9.0	0.0025	15.5	0.0015
3.1	0.0072	6.1	0.0037	9.1	0.0025	16.0	0.0014
3.2	0.0069	6.2	0.0036	9.2	0.0025	16.5	0.0014
3.3	0.0067	6.3	0.0036	9.3	0.0024	17.0	0.0014
3.4	0.0066	6.4	0.0035	9.4	0.0024	17.5	0.0013
3.5	0.0064	6.5	0.0035	9.5	0.0024	18.0	0.0013
3.6	0.0062	6.6	0.0034	9.6	0.0024	18.5	0.0012
3.7	0.0060	6.7	0.0034	9.7	0.0024	19.0	0.0012
3.8	0.0059	6.8	0.0033	9.8	0.0023	19.5	0.0012
3.9	0.0058	6.9	0.0033	9.9	0.0023	20.0	0.0012

If 1 gram of coal is taken and the reading on the photometer is 3.1 cm., then from the table the amount present is 0.0072 gram, and the coal contains 0.7 per cent. of sulphur. A coal should not contain over 1 per cent. of volatile sulphur ; 1.5 per cent. may sometimes be taken as a limit.

In the accompanying diagram the long dash line is the curve produced by the precipitation of barium sulphate where the ordinates are centimeters in depth, and the abscissas are grams of sulphur trioxide when reading with the photometer. The unbroken line is the reciprocal curve and the dotted line is the curve produced by standard silica made from diatomaceous earth.

The silica curve shows the form of curve produced by an absolutely insoluble substance and its variation from the reciprocal curve shows the effect of the cutting out of light by the water itself.



The difference between the silica curve and the sulphate curve represents the solubility of the barium sulphate. This explains why the formula takes the form

$$x = \frac{0.0574}{y + 0.1},$$

when according to optics the denominator should be $(y - a)$ instead of $(y + a)$.

A wide field is open for experiments upon the photometric determination of other precipitates and, in the future, there is no reason why photometry should not take as important a place in chemical analysis as that now occupied by colorimetry.

MT. PROSPECT LABORATORY,
BROOKLYN, N. Y.

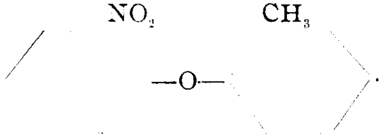
DERIVATIVES OF PHENYLETHER, II.

BY ALFRED N. COOK.

Received August 27, 1901.

IN a paper[1] published a few months since by A. N. Cook and H. W. Hillyer a number of derivatives of phenylether were described which had been prepared by acting on potassium paracresolate with orthobromnitrobenzene, and reducing and oxidizing the resulting compound. During the past six months the work has been extended to orthocresol and metacresol with results as described in the following pages :

2-Nitro-2'-Methylphenylether,



This compound was prepared by the action of orthobromnitrobenzene upon potassium orthocresolate. The reaction is represented by the following equation :

$$NO_2.C_6H_4Br + KO.C_6H_4.CH_3 = NO_2.C_6H_4OC_6H_4.CH_3 + KBr.$$

The potassium orthocresolate was prepared by heating on the water-bath, for several hours, molecular equivalents of orthocresol and potassium hydroxide dissolved in a little water, and then drying in the air-bath until thoroughly desiccated. On cooling, it solidified to a crystalline mass of a light brownish color. It is very hygroscopic.

In the preparation of the ether, molecular equivalents of potassium orthocresolate and orthobromnitrobenzene were heated in an oil-bath. At 137° C., a gentle ebullition began which increased for a few minutes, although the containing flask was removed from the bath, and then gradually subsided. The temperature also rose several degrees during the action. When the action had ceased there remained a copious precipitate of potassium bromide and a supernatant brownish-black liquid. When cool the liquid was

---

[1] *Am. Chem. J.*, **24**, 525-529.