Charcoal, owing to its small percentage of ash, yields a very pure carbide. The only drawback, besides its price, is that it is so light that the gases carry if off to a considerable amount. It is therefore necessary to add from five to ten per cent. more carbon to the mixture if charcoal is used than if coke is used.

We used a soft coal which contained volatile matter 19.84 per cent. and ash 1.48 The mixture with soft coal gave a terrific blaze. The carbide was covered with a large amount of very porous slag in which there was much graphite. The average of results of two runs are : 6.41 pounds per horse power in twenty-four hours and 4.33 cubic feet of gas per pound, which equals 27.75 cubic feet of gas per horse power in twenty-four hours.

We used anthracite coal, which contained volatile matter 7.95 per cent. and ash 4.02 per cent. We made two runs with slacked and two with unslacked lime. There was no appreciable difference in the use of slacked and unslacked lime. The average result of the four runs was : 7.64 pounds per horse power in twenty-four hours and 4.03 cubic feet of gas per pound, which equals 30.79 cubic feet per horse power in twenty-four hours. These results are much lower than those obtained with coke. We can not therefore recommend the use of either anthracite or soft coal for making carbide. The superiority of coke and charcoal over anthracite is probably due to the porosity of the former materials, which must facilitate the volatilization of the carbon in the electric arc, which probably must precede the formation of carbide.

ON THE ACTION OF WAGNER'S REAGENT UPON CAFFEINE AND A NEW METHOD FOR THE ESTIMATION OF CAFFEINE.

BY M. GOMBERG.

Received February 10, 1896.

THE use of iodine in potassium iodide as a general qualitative reagent for alkaloids dates as far back as 1839.[1] It was, however, R. Wagner[2] who first employed it for the quantitative estimation of vegetable bases, and this solution has since been known as Wagner's reagent. He based his con-

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[1] Bouchardat: *Compt. Rend.*, 9, 475.

[2] *Dingl. poly. J.*, 161, 40; *Ztschr. anal. Chem.*, 1, 102.

clusion upon trials with solution of quinine and cinchonine, showing that under approximately similar conditions they always require the same amount of iodine for complete precipitation. Hence empirical factors could be established which would enable one to use a standard solution of iodine for the titration of all such alkaloids as form insoluble superiodides. The method, however, was not frequently employed, for the reason that there was no experimental proof as to the constancy of composition of the precipitates. Moreover, it was noticed that some of the precipitates give up a portion of their iodine to water, *i. e.*, they are not completely insoluble. Hence concordant results could not be obtained. Later, Schweissinger[1] applied this method to the estimation of strychnine and brucine. His results have led him to the conclusion that while the method is very satisfactory for strychnine, it is far from being so for brucine. Recently Kippenberger,[2] in his research upon the isolation and separation of alkaloids for toxicological purposes, has reviewed the subject of the action of Wagner's reagent upon alkaloids, and gives considerable prominence to this as one of the best methods for the estimation of the vegetable bases. His method of procedure was practically the same as that first proposed by Wagner. The alkaloid is dissolved in acidulated water, and to the solution a tenth or twentieth normal solution of iodine in potassium iodide is gradually added until all the alkaloid is precipitated and the supernatant liquid shows a slight excess of iodine. Instead of filtering and washing the precipitate, as was done by Wagner and Schweissinger, Kippenberger allows the precipitate to settle, and either decants or filters off an aliquot portion of the mother liquid for the estimation of iodine not taken up by the alkaloid. The estimation of iodine is always done by means of a standard solution of sodium thiosulphate.

It has been usually assumed, for reasons not entirely clear, that the composition of the precipitates is $Alk.HI.I_2$, *i. e.*, diiodides of the hydriodides of the alkaloids are formed. Of the three atoms of iodine only two can be estimated directly by titration with sodium thiosulphate. The hydriodic acid is supposed to come from the potassium iodide, while the two "superio-

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[1] *Arch. d. Pharm.*, 64, 615, *1885*.

[2] *Ztschr. anal. Chem.*, 34, 317; 35, 10.

dine ''atoms are furnished by the free iodine dissolved in the potassium iodide. The quantity of an alkaloid precipitated by a known volume of Wagner's reagent is calculated on this assumption, 2I : molecular weight of alkaloid : : amount of iodine taken up : $x =$ amount of alkaloid. Schweissinger found that the method of calculation agrees entirely with the theoretical figures for strychnine. Kippenberger has called into question the correctness of this mode of calculation. He, too, assumes that the composition of the precipitates is to be represented by the formula $Alk.HI.I_2$, but he claims that all three atoms of iodine are supplied by the free iodine, and none by the potassium iodide. Therefore the calculation of the amount of alkaloid precipitated is to be done, according to Kippenberger, by the use of the proportion, 3I : molecular weight of alkaloid : : amount of iodine taken up : $x =$ amount of alkaloid.

The hydriodic acid, it is supposed by Kippenberger, results from the interaction of iodine and water,

$$2I + 2H_2O = 2HI + H_2O_2,$$

a reaction which is facilitated or induced by the avidity of the alkaloids to form insoluble periodides of the hydriodides. His reasons for assuming that such a peculiar reaction takes place under the simple conditions of precipitation, are too lengthy to be given here. All his arguments rest upon the assumption that all alkaloids form periodides of uniform composition, $Alk.HI.I_2$, and that the same alkaloid gives always the same periodide. Now, there is no reason, *a priori*, why this should be the case. Jörgenson's[1] extended researches show that different alkaloids, when treated under apparently the same conditions, give periodides of entirely different compositions. Thus, morphine gives with Wagner's reagent $Alk.HI.I_3$;[2] codeine furnishes with excess of Wagner's reagent $Alk.HI.I_4$; and caffeine, as will be shown, gives $Alk.HI.I_4$, etc. It is safe to say that not until we ascertain exactly the composition of the different periodides as produced under the conditions of titrations, will the use of Wagner's reagent for quantitative purposes be placed upon a sound basis.

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[1] *J. prakt. Chem.*, *1870-78*, [2], **2**, 433, etc.

[2] Jörgenson, 1870 : *J. prakt. Chem.*, [2], **2**, 438.

I have dwelt at such length upon this subject, because the method for the estimation of caffeine presently to be described, is based upon experimental evidence which is entirely contradictory to Kippenberger's conclusions. Whatever the cause may be with other alkaloids, his theory as to the production of hydriodic acid from iodine and water, does not hold good in the case of caffeine.

Wagner, in describing his method, gives a list of alkaloids which are completely precipitated by iodine solution, and also mentions that "caffeine, theobromine, piperine and urea are not precipitated at all."[1] His statement, so far at least as caffeine is concerned, has stood since then uncontradicted. It has found its way not only into standard treatises and text-books,[2] but even into periodical literature of recent date. As late as 1894, Kunze,[3] in reviewing the chemistry of caffeine and theobromine, calls attention to this peculiarity of the two alkaloids. The non-precipitation of caffeine by Wagner's reagent has come to be recognized as a distinguishing feature of this alkaloid from almost all other vegetable bases.

And yet this is entirely contrary to actual facts. Instead of forming an exception, caffeine conforms to all the requirements[4] necessary in the application of this test. It is well known that most of the alkaloids as such are insoluble, or only very slightly soluble in water; they require the presence of some acid for their complete solution. In other words, alkaloids in the form of their salts, are soluble in water. Whenever Wagner's reagent is applied for the precipitation of an alkaloid, it is always applied to a solution of some salt of it, preferably acidulated with sulphuric or hydrochloric acid. Therefore, even when strictly neutral salts of alkaloids are employed, there is still the possibility of the formation of hydriodic acid, or rather of the hydriodides of the alkaloid, as for instance, $\text{Alk.HCl} + \text{KI} = \text{Alk.HI} + \text{KCl}$.

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[1] *Loc. cit.* 41.

[2] Prescott, Organic Analysis, p. 80; Allen, Comm. Organic Analysis, Vol. 3, (2), 481; Fluckiger, Reactions, (Nagelvoort's Translation), p. 26; not affected by Wagner's reagent in either neutral or acid solutions; Dragendorff, *1888*, Ermittelung von Giften, says that caffeine gives a dirty brown precipitate. From the text it is not improbable he used iodine in hydriodic acid.

[3] *Ztschr. anal. Chem.*, 33, 23.

[4] This test is perhaps most frequently made in a neutral solution, representing, as customary state, free caffeine and *normal salts* of other alkaloids.

The hydriodide thus produced is at once precipitated as a periodide. Now, it so happens that caffeine is tolerably soluble in water, and it has become customary to work with solutions of caffeine as a free alkaloid, and not in the form of its salts. The question as to whether solutions of free alkaloids are precipitated with Wagner's reagent has not, to my knowledge, been studied. My preliminary experiments in that direction show that at least some alkaloids (morphine, atropine, strychnine, etc.), are precipitated. I have not examined yet whether these periodides are identical in composition with those produced from the salts of the alkaloids. But so far as caffeine is concerned, it is true that a neutral solution of it gives no precipitate when treated with a solution of iodine in potassium iodide. When however the addition of Wagner's reagent is either followed or preceded by the addition of some dilute acid, there is at once thrown down a dark-reddish precipitate, remaining amorphous even on long standing.[1] The composition of this periodide is, as will be shown, $C_8H_{10}N_4O_2.HI.I_4$. It was obtained for analysis in many different ways—by using either caffeine or iodine in excess, and by employing different acids. The periodide produced is, however, always of the same composition. The precipitates were allowed to settle, filtered by means of a pump, washed with water to remove the excess of potassium iodide, dried on porous plates, and finally in a *vacuum* over sulphuric acid.

I. This sample was obtained by slowly adding a solution of iodine in potassium iodide to a solution of caffeine acidulated with sulphuric acid. The iodine was added until the supernatant liquid was decidedly red. The whole was allowed to stand three hours, filtered, washed and dried as described above. The total iodine was estimated in the usual way, *i. e.*, by suspending a weighed sample in water, adding sulphurous acid solution, then silver nitrate and nitric acid; filtered, washed and dried. The "exterior" iodine, *i. e.*, the iodine not as hydriodic acid,

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[1] Almost the same can be said of theobromine, making allowance for the difference of solubility of the alkaloid in water. A saturated solution of it (containing one part of theobromine to 1600 of water) gives no precipitate with Wagner's reagent, but on the addition of a drop of acid there separates in a short time a crystalline periodide. Contrary to usual statements, I find that theobromine in acid solutions gives a heavy precipitate with Wagner's reagent, of a peculiar dirty-blue color.

was estimated by direct titration with standard sodium thiosulphate.

0.2002 gram gave for total iodine 0.2785 gram AgI.
0.2358 " " " exterior " 0.1433 gram I.

II. This sample was obtained by adding to an acidulated solution of caffeine enough iodine to precipitate about one-half of the caffeine present.

0.2563 gram gave for total iodine 0.3591 gram AgI.
0.1659 " " " exterior " 0.0997 gram I.

III. A neutral solution of caffeine was mixed with an excess of Wagner's reagent, and to the mixture dilute sulphuric acid was gradually added so long as a precipitate was produced.

0.4039 gram gave for total iodine 0.5668 gram AgI.
0.1424 " " " exterior " 0.0866 gram I.

IV. Filtrates from I and III, on long standing, gave a deposit of dark-blue needle-like crystals, which were collected, washed and dried as before.

0.7884 gram gave for total iodine 1.1064 gram AgI.
0.4450 " " " exterior " 0.2685 gram I.

V. This was obtained by recrystallizing the amorphous precipitate from methyl alcohol.

0.2890 gram gave for exterior iodine 0.1756 gram I.

VI. Obtained by recrystallizing the amorphous periodide from hot ethyl acetate.

0.4807 gram gave for total iodine 0.6709 gram AgI.
0.2777 " " " exterior " 0.1622 gram I.

Calculated for $C_8H_{10}N_4O_2.HI.I_4$.	Per cent.	Found.					
		I.	II.	III.	IV.	V.	VI.
Total iodine....	76.44	75.12	75.66	75.84	75.83	....	75.40
Exterior iodine.	61.15	60.79	60.11	60.81	60.34	60.76	60.22

When some of the periodide is treated with a solution of sulphur dioxide, and then extracted with chloroform, it furnishes unchanged caffeine.

The composition of this periodide of caffeine appears to be different from that described by Tilden,[1] which he obtained by exposing to sunlight an alcoholic solution of caffeine containing some hydriodic acid. The slow oxidation of the hydriodic acid

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[1] *J. Chem. Soc.*, 18, 99, *1865*.

furnished the iodine, and the compound thus obtained has the composition, according to Tilden, $2(C_8H_{10}N_4O_2HI.I_2).3H_2O$. It is a lower periodide than the one which is obtained when iodine dissolved in potassium iodide is directly added to caffeine, as the latter has the composition $C_8H_{10}N_4O_2.HI.I_4$. Tilden also mentions that by the addition of alcoholic iodine to a solution of caffeine in weak sulphuric or hydriodic acid, he obtained a deposition of black granules, which upon analysis furnished about seventy-five per cent. of total iodine. He says that it probably consists of a compound containing nine atoms of iodine. But there is hardly any doubt that he had the tetra-iodide of caffeine hydriodide.

Properties. When dry the periodide is a violet-blue amorphous powder melting at 213° C. When moist it rapidly loses iodine on exposure to air. It is permanent when dry and suffers but slight loss when heated to 100° C. Two grams heated for four hours at that temperature lost only 0.027 gram = 1.33 per cent. It loses but very little of its iodine when suspended in water, giving up enough iodine to saturate the liquid. The presence of potassium iodide in the water favors the liberation of iodine, but even then it is but slight. The periodide dissolves readily in alcohol, especially when heated, with considerable decomposition into the free base and iodine. It is more soluble in methyl alcohol and suffers less decomposition in that solvent. It can be obtained from methyl alcohol, on spontaneous evaporation of the solvent, in the form of beautiful crystals, with a metallic dark-bluish lustre. When examined under the microscope the crystals appear to consist of six-sided prisms. Ether, whether cold or warm, decomposes it but slightly. The periodide is insoluble in chloroform, carbon disulphide and benzene. It is soluble without decomposition in hot ethyl acetate, from which it separates on cooling as a dark granular crystalline deposit, which melts at 215° C.

Limits of Precipitation. Like most alkaloids, caffeine is precipitated by Wagner's reagent even from very dilute solutions of the base. Although not characteristic, it is yet as delicate a test for caffeine as we have. The limits of precipitation, under the influence of different acids, will appear from the following table. The tests apply to one cc. of the solution mentioned, acidulated with two or three drops of the acid, and to this two drops of Wagner's reagent (twentieth normal) was added.

Dilution.	Sulphuric acid. Five per cent.	Hydrochloric acid. Five per cent.	Nitric acid. Five per cent.	Acetic acid. Five and fifty per cent.	Oxalic acid. Five per cent.	Tartaric acid. Ten per cent.	Citric acid. Ten per cent.
1 : 250	v. heavy.	v. heavy.	v. heavy.	none.	heavy.	slight.	faint.
1 : 1000	v. heavy.	v. heavy.	v. heavy.	.....	heavy.	v. sl.	none.
1 : 1500	heavy.	heavy.	heavy.	.....	sl.	none.	.....
1 : 3000	fair.	fair.	fair.	.....	faint.	.....	.....
1 : 5000	v. sl.	sl.	sl.	.....	.....	.....	.....
1 : 8000	v. sl.	sl.	sl.	.....	.....	.....	.....
1 : 10000	none.	v. sl.	v. sl.	.....	.....	.....	.....

ESTIMATION OF CAFFEINE.

All the methods for the estimation of caffeine depend upon the extraction of the alkaloid by an immiscible solvent from either a dry residue, or from its solution in water. But Spencer[1] has recently shown how difficult it is to remove the alkaloid from its solution in water. According to him, it is necessary to shake out the liquid at least seven times with chloroform, in order to remove caffeine quantitatively. It is usually stated that caffeine does not form any stable salts in a watery solution, and consequently it can be shaken out with immiscible solvents from either alkaline or acid solutions. But this is only relatively true, as will appear from the following illustrations. 1.0085 grams of caffeine were dissolved in sixty cc. of sulphuric acid (1 : 10), and this solution was repeatedly shaken out with chloroform, twenty-five cc. at a time.

10 consecutive portions of chloroform gave a total of 0.3514 gram caffeine
3 additional " " " made a " " 0.4859 " "
3 more additional portions of " " " " 0.5034 " "

The extreme delicacy of the test for caffeine by means of Wagner's reagent, has suggested the possibility of applying this reagent for the quantitative estimation of the alkaloid. Its successful application necessitates, of course, a solution of the alkaloid free from other substances that are precipitated by, or absorb iodine,—a condition requisite in the estimation of any base by

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[1] *J. anal. Chem.*, 4, 390, *1890*.

means of Wagner's reagent. This method gives very satisfactory results, as nearly theoretical as could be expected. I am indebted for the analytical data of the subjoined table to Mr. James W. Knox, holder of the Stearns' Fellowship in the School of Pharmacy. The method of procedure employed by us was practically the same as that used by Kippenberger. Definite volumes of acidulated solutions of caffeine were precipitated with a known volume of iodine in potassium iodide. After complete precipitation an aliquot portion of the supernatant liquid was obtained, either by decantation or filtration, and the excess of iodine was estimated by titrating against a tenth normal solution of sodium thiosulphate. The precipitation is best performed in a tall test-tube on foot, and the solution for titration is removed directly by immersing the end of the burette into the liquid and applying suction at the upper end. When it is desirable to filter off an aliquot portion, a filter of glass-wool and asbestos gives very satisfactory results.

We have tested the method on solutions of caffeine acidulated with sulphuric acid, the solutions being of different strengths, namely: containing 0.25 per cent. of caffeine, 0.50 per cent., 0.75 per cent., and 1.00 per cent., respectively. We have varied in different series of experiments the amounts of Wagner's reagent, employing just the theoretical quantities, a small and large excess above that, as well as quantities below those required by the theory. Columns I, II, III, and IV give the results obtained by allowing the solutions to stand for an hour before decanting an aliquot portion for titration; column V shows the results obtained when the liquid for titration was filtered off within five minutes after the addition of Wagner's reagent. The results are calculated on the basis that the periodide has the composition $C_8H_{10}N_4O_2.HI.I_4$. The amount of alkaloid is calculated from the amount of iodine used up, by the formula,

$$4I : C_8H_{10}N_4O_2 :: 506 : 194;$$

i. e., one part of iodine represents 0.3834 parts of caffeine. Or, one cc. tenth normal iodine = 0.00485 grams caffeine.

The results presented below show that the estimation of caffeine by this method is very exact. The best results are obtained

	I.			II.			III.			IV.			V.		
	Solution containing 0.25 per cent. of caffeine.			Solution containing 0.50 per cent. of caffeine.			Solution containing 0.75 per cent. of caffeine.			Solution containing 1.00 per cent. of caffeine.			Solution containing 0.50 per cent. of caffeine.		
Wagner's reagent employed.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.	Taken.	Found.	Per cent. recovered.
Theoretical quantity + 2 cc.	0.0600	0.0591 0.0589	98.33	0.1200	0.1175 0.1175	97.82	0.1500	0.1481 0.1471	98.40	0.1200	0.1182 0.1179	98.38	0.1200	0.1154 0.1165	96.78
1⅓ theoretical quantity.	0.0750	0.0749 0.0749	99.88	0.1200	0.1191 0.1189	99.17	0.1500	0.1489 0.1485	99.13	0.1200	0.1191 0.1187	99.12	0.1200	0.1196 0.1197	99.75
Twice the theoretical quantity.	0.0500	0.0502 0.0506	100.80	0.0800	0.0805 0.0789	99.63	0.1200	0.1184	98.67	0.1100	0.1091 0.1091	99.18	0.0800	0.0802 0.0791	99.63
One-half of the theoretical quantity.	0.0750	0.0363 0.0363	48.40	0.1600	0.0794 0.0794	49.62	0.2250	0.1107	49.20	0.2000	0.1067 0.1067	53.35	0.1600	0.0791 0.0791	49.44

when iodine is in considerable excess, as is evident from the figures obtained where one and one-third and twice the theoretical quantities of Wagner's reagent were used. All the results in the table were obtained on solutions of caffeine acidulated with sulphuric acid, the acidulation being tolerably strong, about one cc. of the concentrated acid to fifty cc. of the liquid. Experiments upon the influence of the acid indicate that a large excess of sulphuric acid interferes to some extent with the reaction. The amount of recovered caffeine falls as low as ninety-five per cent. of the quantity taken, when four cc. of the concentrated acid to fifty cc. of the liquid are used. The results are also not very uniform and concordant. The fact that the precipitation of caffeine by Wagner's reagent is more delicate in presence of hydrochloric acid than any other acid would make it advisable to employ that acid in quantitative estimation of the base by iodine.

This method could easily be employed for the estimation of the alkaloid in caffeine-bearing drugs. Of course, it is necessary to have the final solution of the alkaloid in water as free as possible from other substances that may be precipitated by Wagner's reagent. The estimation of caffeine by this method is likely to give higher results than have hitherto been obtained. The following procedure is recommended.[1] The drug is thoroughly digested with water for some time, by the aid of heat, cooled, and made up to a definite volume, and filtered. An aliquot portion of the filtrate is treated with lead acetate, the precipitate allowed to settle, and filtered. The whole of the filtrate, or a given portion of it, is treated with hydrogen sulphide to remove the lead, and filtered. This filtrate, after boiling off the hydrogen sulphide, is divided into two equal portions, and each treated with a definite volume of the standard iodine solution,—the first portion without the addition of any mineral acid, the second with the addition of hydrochloric or sulphuric acid. After five to ten minutes' standing the excess of iodine is estimated in each of the two solutions, as described above. The first portion, containing no other but some acetic acid, serves to indicate whether the filtrate from the lead sulphide contains any other materials besides caffeine that are likely to be

[1] These directions are in part those given by Spencer, *1890: J. anal. Chem.*, 4, 390.

precipitated by Wagner's reagent,—for caffeine itself is not precipitated by it even in presence of tolerably strong acetic acid. If any absorption of iodine be found in the first portion, then that quantity is to be subtracted from the amount of iodine taken up by the second portion ; the difference represents the iodine used up in the formation of the periodide of caffeine. The amount thus used up, multiplied by 0.3834, gives the amount of caffeine in that particular portion of the liquid.

ANN ARBOR, MICHIGAN.

ON THE FORMATION OF ANTIMONY CINNABAR.

BY J. H. LONG.

Received February 15, 1896.

THE composition of the pigment known as antimony cinnabar has been stated by several different formulas, as may be seen by consulting the leading hand-books of chemistry. The substance was usually considered as a mixture of sulphide and oxide or as an oxysulphide with the formula Sb_2S_2O. The formula, Sb_2S_3, is found also in some of the older works, and Baubigny[1] has shown that this is undoubtedly the correct one. Experiments made by myself and described in this Journal, in February, 1895, led me to adopt the same formula.

The compound is usually prepared by boiling a solution of antimony chloride or tartrate with sodium thiosulphate or crude calcium thiosulphate. As obtained from the acid solution of the chloride, the product is not pure and not of constant composition, being frequently mixed with oxychloride. This mixture is a mechanical one and analysis made from it has no value in establishing a formula. The precipitate obtained by boiling a mixture of pure solutions of tartar emetic and sodium thiosulphate, on the other hand, has a constant composition, and numerous analyses I have made of it in the past year lead to the formula already given.[2]

By analogy with other formulas established in the paper referred to I suggested there that the reaction between the tartrate and thiosulphate may be represented by this equation :

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[1] *Compt. rend.*, October 22nd, 1894.

[2] *Loc. cit.*