no longer sinks to the bottom, but the whole mass partially gelatinizes and becomes dirty brown. A clear filtrate free from tannin and mercury can then be readily obtained.

The results in the ash column show that a certain amount of the ash present in the extract is held back, but this error is quite constant and so small as to have little influence on the result. Although the time required for the analysis of a tannin-extract by this method is somewhat longer than with hide-powder, still the uniform results obtained more than compensate for this, and, at the most, an analysis will not take more than two days. A number of analyses can be made at a time by adapting a shaker so as to hold several 100 cc. sugar flasks, which are of a convenient size for this work.

THE ESTIMATION OF SULPHUR IN REFINED COPPER.[1]

BY G. L. HEATH.

Received September [illegible], 1 95.

SEVERAL general methods for the estimation of sulphur in copper have been published, most of which are defective, or not accurate for all classes of work.

It is the writer's purpose to call attention to these processes, and then to present the results of some experiments, and an improved method, devised especially for the determination of traces of sulphur.

R. Fresenius[1] proposed to treat twenty grams of copper with strong nitric acid, nearly neutralize with ammonia, add a few drops of barium nitrate and allow to stand for several hours. As stated by the same authority, very small quantities can not be separated in this way, since barium sulphate is somewhat soluble in copper nitrate.

For small amounts of sulphur, W. Hampe's "chlorine" process has been recommended. This consists in heating thirty grams of the metal in a glass tube in a current of pure, dried chlorine gas. The sulphuric acid evolved, is absorbed by water saturated with chlorine.

From personal experience, the method is not judged to be a

---

[1] Read at the Springfield Meeting.

[2] *Ztschr. anal. Chem.*, 13, 223.

very accurate one, for there are two or three possible sources of error.

1. The existence of the sulphur in different forms.
2. The incomplete removal of all oxygen and other impurities, from the chlorine gas.
3. The occasional formation of a layer of melted chloride, which may prevent the complete evolution of sulphur and combustion of copper.

A third method involves the use of potassium permanganate.

A fourth, and apparently, the most direct and satisfactory one, consists in dissolving ten grams of copper in nitric acid, or in a mixture of nitric with a little hydrochloric acid, and then precipitating the sulphuric acid directly from a hydrochloric acid solution, after removing all the nitric acid by repeated evaporation.

Upon this principle depends the method of H. J. Phillips.[1]

But the writer has repeatedly attempted to test refined copper by the last method, without obtaining any precipitate of barium salt. There should have been at least a trace of precipitate due to sulphur in the chemical reagents.

Though no refining on the large scale has ever produced metal in which a chemist could not find a trace of impurity, yet the best American refined copper of to-day, contains such a minute amount of sulphur, that a very delicate and accurate method is required for its estimation.

In order to test the influence of copper chloride and free hydrochloric acid upon barium sulphate, some experiments were made with solutions of pure copper chloride, and sulphuric acid.

It is a well known fact that certain substances interfere with the precipitation by barium chloride, and that barium sulphate is somewhat soluble in certain acids, and in solutions of copper.

The work of R. Fresenius,[2] F. W. Mar,[4] and others, has indicated that an excess of hydrochloric acid promotes the complete separation of barium sulphate, a conclusion rather contrary to earlier opinions.

[1] *Chem. News*, 62, and *J. Anal. Appl. Chem.*, 5, 53.

[2] *Ztchr. anal. Chem.*, 9, 52 and 62, also Fres. Quant. Anal., Am. Ed. p. 139.

[3] *Am. J. Sci.*, 41, April 1891, also *J. Anal. Appl. Chem.*, 5, 278.

Mr. Mar states, as the writer has also noted, that the precipitation of minute quantities of barium sulphate is very much slower than that of large amounts.

Since the barium sulphate is not absolutely insoluble in water or dilute acid, the amount which would remain dissolved by a large volume of solution is appreciable, and cupric chloride may considerably influence the solubility.

As far as the time permitted, the experiments were carried out in two series; those analyses marked *a*, containing but a few drops of free hydrochloric acid, and those marked *b*, *c*, or *d*, about three and a half per cent. by volume of the same acid of 1.20 sp. gr.

Stock solutions were prepared as follows:

a. Standard sulphuric acid—1 cc.=0.00245 gram $BaSO_4$.

b. Cupric chloride solution—100 cc.=10 grams copper.

The solution used for all the experiments (except Nos. 12 *c*. and 12 *d*) was made by dissolving 100 grams of a very pure refined copper in 400 cc. of pure nitric acid, (sp. gr. 1.42), then precipitating the silver with a few drops of hydrochloric acid and filtering it off. The solution was then evaporated to dryness, and the evaporation repeated four times, with the addition of hydrochloric acid each time. The heat was continued until the chloride melted. The salt finally dissolved in water to a clear, faintly acid solution, which was diluted to one liter.

The slight trace of sulphur in the copper, was not any more than that found in the chemical reagents.

Ten grams of the copper yielded, by the author's method, only 0.0017 gram of barium sulphate, and the acids required for solution, gave 0.003 gram, for which allowance was made in the table of results.

c. As a check, some of the same copper was deposited by electrolysis from a nitric acid solution, and the pure plate was then redissolved, and after further treatment, the solution was used for experiments 12*c* and 12*d*, in which one cc. standard sulphuric acid was added to the diluted copper solution.

The measured portions of copper salt, water and acid were placed in beakers and the standard sulphuric acid run in from a burette. The liquids were heated to boiling, treated with two to five cc. of a saturated solution of barium chloride, stirred, and allowed to stand at the temperature of the room for the number of hours specified in the table.

The precipitates of the tests marked (*b*, *c*, *d*,) were washed first with five cc. of dilute hydrochloric acid, (one part acid to twenty of water) and then with hot water. The ones marked (*a*) were washed with hot water only, and in two or three cases, a trace of copper was not washed out. (See experiments 11*a*, and 15*a*).

At least a few drops of dilute acid should be always used in the first washing by decantation.

The results are tabulated according to the degree of dilution, and the weight of copper in the solution:

TABLE I.

ONE-TENTH GRAM OF COPPER IN SOLUTION. TOTAL VOLUME OF SOLUTIONS SEVENTY CC.

Faintly acid two-tenths free hydrochloric acid.					Strongly acid two and a half cc. hydrochloric acid added.				
		Gram barium sulphate.					Gram barium sulphate.		
No.	Time in hours.	Taken.	Found.	Difference.	No.	Time in hours.	Taken.	Found.	Difference.
1*a*	24	0.0025	0.0027	+0.0002	1*b*	24	0.0025	0.0027	+0.0002
2*a*	24	0.0123	0.0127	+0.0004	2*b*	24	0.01235	0.0124	0.0000
3*a*	24	0.04905	0.0489	—0.00015	3*b*	24	0.0491	0.0497	+0.0006

TABLE II.

ONE GRAM OF COPPER IN SOLUTION. TOTAL VOLUME OF SOLUTIONS, 350 CC.

Slightly acid two-tenths cc hydrochloric acid.					Strongly acid 12.5 cc. hydrochloric acid.				
		Gram barium sulphate.					Gram barium sulphate.		
No.	Time in hours.	Taken.	Found.	Difference	No.	Time in hours.	Taken.	Found.	Difference.
4*a*	24	0.0029	0.0026	—0.0003	4*b*	24	0.0029	0.0009	—0.0020
5*a*	24	0.0126	0.0115	—0.0011	5*b*	24	0.0126	0.0101	—0.0025
6*a*	24	0.0495	0.0446	—0.0049	6*b*	34	0.0495	0.0385	—0.0110
6*a*	72	0.0495	0.0490	—0.0005	6*b*	72	0.0495	0.0493	—0.0002
7*a*	72	0.2455	0.2445	—0.0010	7*b*	72	0.2462	0.2500	+0.0038

TABLE III.

TWO AND A HALF GRAMS OF COPPER IN SOLUTION. TOTAL VOLUME 350 CC.

Slightly acid two-tenths cc. hydrochloric acid.					Strongty acid 12.5 cc. hydrochloric acid added.				
		Gram of barium sulphate.					Gram of barium sulphate.		
No.	Time in hours.	Taken.	Found.	Difference.	No.	Time in hours.	Taken.	Found.	Difference.
							0.0046	0.0000	—0.0036
8*a*	24	0.0036	0.0007	—0.0029	8*b*	24	0.0936	0.0006	—0.0030
					8*c*	72	0.0036	0.0014	—0.0022
9*a*	72	0.0135	0.0129	—0.0006	9*b*	72	0.0135	0.0128	—0.0007
					9*c*	140	0.0145	0.0131	—0.0014
10*a*	72	0.0502	0.0496	—0.0006	10*b*	24	0.0502	0.0493	—0.0009
					10*c*	72	0.0502	0.0492	—0.0010
					10*d*	140	0.0502	0.0501	—0.0001
11*a*	72	0.2470	0.2505?	+0.0035	11*b*	72	0.2470	0.2486	+0.0016

TABLE IV.

TEN GRAMS OF COPPER IN SOLUTION. TOTAL VOLUME 700 CC.

Faintly acid one-half cc. hydrochloric acid.					Strongly acid twenty-five cc. hydrochloric acid added.				
		Gram barium sulphate.					Gram barium sulphate.		
No.	Time in hours.	Taken.	Found.	Difference.	No.	Time in hours.	Taken.	Found.	Difference.
		0.0074	0.0000	—0.0074					
12*a*	24	0.0074	0.0000	—0.0074	12*b*	24	0.0074	0.0000	—0.0074
					12*c*	140	0.0057	0.0005	—0.0052
					12*d*	"	0.0057	0.0004	—0.0053
13*a*	72	0.0170	0.0102	—0.0018			0.0165	0.0014	—0.0151
					13*b*	24	0.0165	0.0013	—0.0153
14*a*		lost			13*c*	72	0.0165	0.0051	—0.0114
					14*b*	24	0.0540	0.0502	—0.0038
					14*c*		0.0540	0.0400	0.0140
15*a*	72	0.2509	0.2551?	+0.0047	15*b*	24	0.2500	0.2389	- 0.0111
						72	0.2500	0.2436	—0.0064
						140	0.2500	0.2474	0.0026

The results, given in Table I., show that if the total volume of a solution is not over 100 cc. the barium sulphate is completely precipitated, whether the liquid is strongly acidified or not.

Table II: If the volume of the solution is increased to 350 cc. and the copper to two and a half grams, the precipitation is complete, even then, under the given conditions, in 72 hours with the exception of the analysis containing but a trace of sulphuric acid.

Tables III and IV : In the presence of as much as ten grams of copper in solution, the deposition becomes very slow indeed, as the results prove, and the strongly acidified solutions, at least retain appreciable amounts of barium sulphate.

Since the solubility of barium sulphate varies according to the conditions somewhat, the figures given by Fresenius, F. W. Mar, and others would not express the true effect of the water and dilute hydrochloric acid if the conditions of acidity, temperature, dilution, etc., were not the same. So a few experiments were made to determine the solvent effect of the water and acid alone.

Analyses 16-20 indicate that a part at least of the deficiency noted in the other tables is due to the solubility of the precipitate in the large volume (700 cc.) of dilute acid.

TABLE V.

No.	cc. of hydrochloric acid.	Temperature during settling.	Total volume.	Time in hours.	Gram barium sulphate. Taken.	Found.	Difference.
16	25	20° C.	700	48	0.0025	0.0008	—0.0017
17	25	20° C.	700	48	0.0123	0.0086	—0.0037
18	25	20° C.	700	48	0.0490	0.0470	—0.0020
19	2 cc. + 5 grams ammonium chloride.	75° C.+	70	3	0.0490	0.0487	—0.0003

Fresenius[1] states that 1,000 parts of cold hydrochloric acid containing 3 per cent. dissolve 0.06 parts $BaSO_4$.

Other experiments proved, however, that if a solution be kept at a temperature above 75° C., after the addition of barium chloride, the separation of barium sulphate is far more rapid and complete.

Cupric chloride appears to retard the deposition, especially when strongly acidified.

Direct precipitation in a moderately acid solution of this salt is determined to be sufficiently accurate for mattes and crude copper, but the separation of minute amounts of barium sulphate, from a very large volume of chloride solution, is too uncertain to permit the use of such a method for the detection and estimation of traces of sulphur in the best modern refined copper.

---

[1] F. Quant. Anal., 1st Am. Ed., p. 139, from Anal. Chem., 9, 62.

In 1889 the late Dr. L. M. Norton and the author of this paper devised and adopted a simple method, which has been improved by the latter, and has given very accurate results.

The complete precipitation of the barium sulphate is made possible in every case by first removing the copper electrolytically and then treating the solution as in the following scheme:

Take for analysis sufficient copper to yield a weighable amount of barium sulphate—ten grams will usually be enough.

Dissolve in a large beaker, placed over an alcohol flame, by means of a mixture of 60 cc. nitric acid (1.42 sp. gr.) and 15 cc. of hydrochloric acid (1.20 sp. gr.).

When dissolved, raise the lamp wick and evaporate nearly to dryness, then evaporate again after adding 50 cc. strong nitric acid.

Repeat this operation with another portion of the same acid, then redissolve in 300 cc. of water, and add a little nitric acid if a trace of basic salt remains undissolved.

The addition of hydrochloric acid and the consequent evaporation with nitric may be dispensed with, if experiment shows that nitric acid alone will oxidize all the sulphur in the class of material operated upon.

Next, pour the liquid through a small filter into a 700 cc. beaker and dilute with distilled water to 600 cc. or more.

Introduce as a negative electrode a large cone, or as is more convenient, a sheet of platinum, 4 by 5 inches.

Any wire or small piece of platinum foil will serve as a positive electrode.

Cover the beaker with glass and connect the electrode, preferably with an Edison incandescent lamp circuit.

The current from two sixteen candle-power lamps, coupled in parallel, will deposit the copper in one night.

When the liquid is colorless, or nearly so, remove the electrodes and wash them with distilled water, allowing the water to run into the main solution.

Pour off the liquid, if clear, from any bits of spongy copper, washing these on a small filter.

In order to prevent the escape of any sulphuric acid during subsequent evaporation, add, at this point, one-tenth gram dry, pure sodium carbonate, (or a half gram for crude copper).

Evaporate the solution to dryness, as rapidly as possible without loss, in a No. 3 or No. 4, porcelain casserole. An alcohol lamp should be used, and the dish protected from dust. The evaporation may be completed on the water-bath, but if the dish is covered near the end of the operation and the flame regulated, there need be no loss by spattering, though the liquid be taken to dryness over the lamp. As soon as the salts in the dish are dry, heat the covered casserole quite strongly, with the lamp held in the hand, until the acid ammonium nitrate suddenly volatilizes, and then allow it to cool.

At this point is the only danger of loss of sulphur, and the heat should be just high enough to volatilize the nitrate. This heating may possibly be omitted if there is but a trace of ammonium nitrate in the dish. (See experiment 19).

Add to the residue, ten cc. strong hydrochloric acid and five cc. water, and evaporate to dryness on the water-bath. Repeat the process and then add one cc. of strong hydrochloric acid, add fifty cc. of water and dissolve, filter into a small beaker and wash the filter with hot water.

If the copper is known to be high in sulphur, the solution may be diluted to 150 cc. or more.

The only impurity of copper which might interfere with this method is lead. If lead is present, it will mostly remain in solution and be deposited on the plate, but if any lead sulphate remains on any of the filters, they must be boiled with a little solution of pure sodium carbonate, the solution filtered, and the sulphuric acid recovered from the acidified liquids as barium sulphate.

Heat the solution of sodium sulphate to boiling, precipitate with a slight excess of barium chloride, and allow the precipitate to settle twenty-four hours, unless the results are desired at once, in which case the precipitation may be completed inside of three hours, by keeping the liquid at a temperature not less than 75° C. during that time.

The acids and distilled water, used in the analysis, should be measured, and a blank analysis carefully made by evaporating with the pure soda, and the trace of barium sulphate deducted from that of the analysis proper. Exp. 20–22 are three comparative analyses from the writer's note-book.

TABLE VI.

COPPER ANALYSIS.

		Per cent. sulphur.		Per cent. sulphur.
20	Direct precipitation	0.0000	Author's method	0.0023
21	" "	0.6000	" "	0.6500
22	" "	0 to 0.0050	" "	(1) 0.0112
22	Chlorine method	0.0189?		(2) 0.0094

It is evident that the method just detailed, is extremely well adapted to the analysis of refined copper.

The sulphur in the metal is brought into solution, and finally precipitated in a pure condition without loss, and a blank analysis is possible under the same conditions. The difference between the two results, expresses the true quantity of sulphur present.

Another chemist stated sometime ago that he, also, had been obliged to try a similar plan. The author has, however, worked out the foregoing process in its improved form independently, and in presenting this standard method, desires to express his indebtedness to the gentleman who has so kindly consented to read the paper before the assembly.

ACIDIMETRIC ESTIMATION OF VEGETABLE ALKALOIDS. A STUDY OF INDICATORS.[1]

BY LYMAN F. KEBLER.

Received September 9, 1895.

THE titration of alkaloids with volumetric acid solutions has been evolved from the study of the basicity of the alkaloids on the one hand, and from their behavior with indicators on the other. The method appears to have been developed somewhat spasmodically from quite an early period. As early as 1846 M. Schlössing[2] proposed the method and applied it to the titration of nicotine with a view of establishing its equivalent; using sulphuric acid and litmus in his work. Sixteen

---

[1] Read at the Springfield meeting.

[2] *1847, Comp. rend.*, **23**, 1142; *1847, Ann. Chim. Phys.* [3], **19**, 230; Chem. Gaz., **5**, 41; Am. J. Pharm., **19**, 68.