date *in the cold*, allows to stand, at the temperature of the room, over night, and titrates in the morning. The details of these modifications are given in the 1894 report of the Association of Official Agricultural Chemists, published at Washington, D. C. Whatever modification may be used, the volumetric method will be found much quicker than the gravimetric, and, after a little experience, fully as reliable.

PHILADELPHIA, Pa.

ON THE ESTIMATION OF SULPHUR IN PYRITES.[1]

BY G. LUNGE.

Received December 20, 1894.

UNDER the above title, Mr. T. S. Gladding (This JOURNAL, June, 1894), has published several modifications of the wet assay of pyrites which call for some comment on my part, since these modifications purport to be improvements on my method, contained in the "Alkali-makers' Handbook," and extensively employed in all countries.

Some of Gladding's modifications are of a less important character, and these can be passed in review very briefly. He does not, like myself, test the sample with its natural moisture, estimating the latter in a special sample, but he dries the whole sample and weighs it out in that state. He employs a whole gram of pyrites, I only half a gram; and I do so purposely, because the washing of the precipitates is much easier, and consequently the results are more reliable with the smaller than with the larger quantity. In lieu of the mixture of acids employed by me (three volumes of nitric acid of sp. gr. 1.42 and one volume of fuming hydrochloric acid) Gladding decomposes the pyrites with a solution of bromine and nitric acid. The prescription for that solution is not correct as printed, for seventy-five grams of potassium bromide can not possibly be dissolved in fifty grams of cold water, or anything like that quantity, but this may be a clerical error, which does not matter very much, as ultimately the solution is diluted to 500 cc. I will say at once that the bromine solution works well, but no better than the acid mixture according to my prescription.

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[1] Read at the Boston Meeting, December 28, 1894.

A more important modification is the following: It is well known that in the presence of iron the precipitate formed by barium chloride in a solution of sulphates can not be freed from iron, and that the results of the estimation of sulphur in this case are too low; in my publication of 1879 (*Ztschr. anal. Chem.*, **19,** 419) I found on the average 0.19 per cent. too little sulphur, unless the iron had been previously removed from the solution. Fresenius has also worked on this subject, and Jannasch and Richards, in 1889, completely elucidated it by proving that a double sulphate of barium and iron was formed in this case. Gladding gives a similar explanation, without mentioning the more complete investigations of his predecessors, which would have saved him the trouble of working out the matter for himself. I had already long ago dealt with that difficulty by proposing, in 1889, that method which was afterwards embodied in the "Alkali-makers' Handbook," *viz.*, precipitating the iron by ammonia, washing the ferric hydroxide, and precipitating the sulphate in the filtrate by barium chloride. Gladding asserts, however, that "the most careful washing failed to wash out all the sulphur from the ferric hydroxide," and he therefore proposes to wash the hydroxide as well as possible and to dissolve it afterwards in diluted hydrochloric acid, thereupon treating that solution with barium chloride: evidently with the tacit assumption that the small-quantity of sulphide present in that solution is accurately enough estimated as barium sulphate, in spite of the large quantity of iron present; but that assumption is far from self-evident, nor does it actually represent the truth, as we shall see.

It is quite evident that Gladding, although he knows and quotes the "Alkali-makers' Handbook," and although he entirely adopts the prescription given there (page 93) for the *precipitation* of the ferric hydroxide, which deviates not unessentially from those previously given by Fresenius and others, has not completely followed the instructions for the *washing* of the precipitate given immediately after in the following words: "Filter hot, and wash on the filter with hot water, avoiding channels in the mass, but so that the whole precipitate is thoroughly *churned up* with the water each time." Many hundreds of pyrites tests made in my own and other laboratories have proved that by following the above instructions the washing of the ferric hydroxide is accomplished in from half an hour to an hour; that the number of washings need not exceed five, and the bulk of the liquid, apart from the original filtrate, need not exceed 100 to 150 cc., and *that no trace of sulphur is left in the ferric hydroxide*, as evidenced by drying the precipitate, fluxing it with pure soda, dissolving it in water, and testing the solution for sulphate. It is true that the students in my laboratory have sometimes failed to get out all the sulphur, but in *every* case through having washed in the usual way, instead of that described above; and the same men have succeeded in *every* case, after their attention had been drawn to this point.

There is another difference between Gladding's and my own manner of proceeding. I prescribe heating the solution of the sulphate to the boiling-point, as well as that of the barium chloride, adding the latter to the former all at once, allowing to stand for half an hour only, and then at once filtering and washing while the liquid is quite hot. I had convinced myself that under these circumstances the precipitate filters most easily, and no barium sulphate whatever subsequently separates from the filtrate. Gladding, however, not merely adheres to the old and useless prescription of letting the liquid stand over night after the precipitation, but he adds to this a novel and most tedious way of effecting the precipitation, *viz.*, adding fifty cc. of barium chloride solution quite slowly, one drop per minute. This will take about an hour, instead of a few seconds, as in my method.

I considered it my duty to find out whether the method recommended by Gladding is better than mine, or inferior to it, or equivalent with it; and in the last case, which of the two is easier and quicker to execute. For this purpose a sample of Spanish pyrites was selected which was triturated as usual and mixed in the most careful manner. The tests were made by one of my demonstrators, H. von Keler, under my constant personal supervision. First of all the sample was tested exactly according to the method laid down in the "Handbook," with the following results: 50.17; 50.42; 50.20; 50.23; 50.19; average, 50.24 per cent. The insoluble amounted to 1.42 per cent; the moisture to 0.47 per cent. I abstain from reducing the percentages to the dry state, as being unnecessary in this case.

As the next step, a number of samples were decomposed by Gladding's mixture of bromine solution and nitric acid. We found his prescription in this item to be perfectly correct; it is not feasible to hasten the process (which is much lengthier than that used by myself), for instance, by filling the water-bath from the first with hot water. Any attempt to do such a thing ends in an over-violent reaction, and a loss by spurting and separation of free sulphur. We tested, of course, our bromine and potassium bromide, and found them quite free from sulphuric acid.

Three of the samples thus decomposed, according to Gladding, were precipitated exactly according to his method (one hour's precipitation, twelve hours' settling), another three samples according to mine (precipitating all at once and filtering after half an hour). The results were:

Gladding's Method.	Lunge's Method.
50.24	50.24
50.24	50.22
50.30	50.28
50.26	50.25

We see that both methods of precipitation give identical results, and these also entirely agree with the tests made from the first according to the "Handbook" method, *viz.*, 50.24. The conclusions to be drawn therefrom are: 1. Since both methods of precipitation yield the same result, my expeditious method of precipitation and filtration, which, inclusive of washing, takes about an hour, is preferable to Gladding's method, requiring about twelve hours. 2. Since Gladding's bromine method for decomposing pyrites yields results identical with that prescribed by myself, there is no reason for abandoning the latter and adopting a more tedious method, unnecessarily employing such a disagreeable reagent as bromine.

I understand from a private communication of Mr. Gladding's that he attributes the greatest value to his manner of precipitating the barium sulphate, and that in his opinion by operating in my way barium chloride is always carried down with the sulphate, making the results too high by 0.20 to 0.40 per cent. It would have been most remarkable if that point had been overlooked in the many thousands of tests made according to my methods by perhaps a hundred different chemists; but in order not to incur any reproach, I had this point put to another searching investigation. Mr. W. Jackson made five most careful tests of another sample of pyrites, decomposing and otherwise treating them absolutely in the same way, but making the precipitation in two cases by Gladding's, and in three cases by my method. The results were:

	Lunge's Method.		Gladding's Method.
	50.59 per cent.		50.60 per cent.
	50.63 " "		50.66 " "
	50.56 " "		....
Average,	50.59 " "	Average,	50.63 " "

This affords another thorough refutation of Gladding's assertion.

In all analyses made up to this point the ferric hydroxide had been precipitated and washed five times, exactly in the way described by me; in every case it had been afterwards tested by fluxing with soda, but no trace of sulphur had ever been found. This furnished an additional (although unnecessary) proof that Gladding's assertion in that respect is equally unfounded, and that the treatment described by him (dissolving the ferric hydroxide in hydrochloric acid and precipitating by barium chloride) is quite useless, when observing the precautions in washing, pointed out by me. Still I thought it advisable to find out how Gladding's process would work in cases where, by some mistake, a little sulphur had been left in the hydroxide, and I grant that in important cases the latter ought to be tested in some way or another for any sulphur left behind. I further grant at once that in this case Gladding's method, as described, is more expeditious than mine: drying the ferric hydroxide, detaching it from the paper, mixing it with pure sodium carbonate, fluxing it in a platinum crucible (in such manner that no sulphur from the gas can get into the mass, *e. g.*, in a hole made in asbestos cardboard), dissolving in water and precipitating the sulphur by barium chloride. It is hardly necessary to say that I did not choose this plan without first considering the very simple method described by Mr. Gladding; but I rejected it, since Fresenius had proved that barium sulphate is very distinctly soluble in an acid solution of ferric chloride. But as Gladding now asserts that the direct solution of the ferric hydroxide in hydrochloric acid yields accurate results, it became incumbent upon me to examine this statement.

Eight samples of our pyrites were decomposed, and the ferric hydroxide was precipitated under absolutely equal conditions of dilution, temperature, and quantities of reagents. The washing was purposely not continued as far as it ought to have been; and as some previous experiments had shown that no uniform degree of exhaustion can be attained by incomplete washing, we estimated in all cases the *total* sulphur, separating, of course, that which was found in the filtrate and that which was left with the ferric hydroxide. Four of the eight samples were treated by Gladding's prescription, and four by my own system. The results were:

Lunge (fluxing with sodium carbonate).			Gladding (dissolving in hydrochloric acid)		
Filtrate.	Precipitate.	Total.	Filtrate.	Precipitate.	Total.
49.64	0.60	50.24	48.98	1.03	50.01
49.36	1.01	50.37	48.84	1.39	50.23
49.07	1.21	50.28	49.02	1.07	50.19
49.25	1.04	50.29	49.30	0.73	50.03
Average,		50.29	Average,		50.09

This proves that Gladding's method does not, in this particular, give accurate, but *low* results (by 0.20 per cent.); with less complete washing the discrepancy would evidently have been even greater. The total sulphur found by my process, on the other hand, agrees quite satisfactorily with the correct analyses quoted before.

The final conclusion of this investigation must be: That in most points Gladding's method is correct, but in *not a single case* more so than my method; his modifications can not be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever. In one point which forms the principal novelty in Gladding's process, he is decidedly *wrong*. It is not true that it is unavoidable to leave any sulphur in the ferric hydroxide; on the contrary this is very easy to avoid. If it has, after all, happened by incorrect manipulation, Gladding's plan will *not* get out all the sulphur, but my plan (fluxing with soda) must be adopted.

I have shown that there is not a single point recommended by Gladding, in deviation from my method, which is fit for adoption, and I must conscientiously advise my brother chemists to adhere to the method just as I have laid it down in the "Alkali-makers' Handbook."

In conclusion I would add that I have also tried the method recommended by F. Johnson (*Chem. News*, *1894*, **70**, 212), omitting to precipitate the iron, but reducing it by sodium hypophosphite to the state of protochloride. Even when working precisely as described by the author, the results were so widely off the truth, that I can make nothing whatever of this plan.

IMPROVEMENT IN THE MANUFACTURE OF ACETONE.[1]

BY E. R. SQUIBB, M.D.

Received January 17, 1895.

THE increasing use of acetone as a chemical solvent, and especially the relation of acetone to the manufacture of chloroform, gives importance to any improvement in its production.

Up to this time the writer knows of no process of manufacture except by the destructive distillation of acetates at high temperature. The acetates are charged into stills and heated as long as they yield any acetone. Then the acetates being decomposed to waste carbonates are discharged and the stills recharged with fresh acetate, making an interrupted process of repeated charging and discharging and heating and cooling. This process is very old; but two patents have been taken out in this country on some details of the process and apparatus.

The writer proposed to himself to make acetone directly from acetic acid by a continuous process, and has accomplished that object.

In Gmelin's Handbook of Chemistry, Cavendish Society edition, *1853*, **8**, 291, under the head of decomposition of acetic acid by heat, much work is given where the vapor of acetic acid was

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[1] Read before the N. Y. Section, January 11, 1895.