experiments made by Smith (*Ztschr. anorg. Chem.*, **1**, 360), with these metals and solutions of silver, gold, and mercury salts. It is further additional comparative evidence of the conduct of the metals of this subdivision of group VI. Of the behavior of chromium in this direction we have no experimental evidence, but of uranium it is known that it reduces salts of tin, platinum, gold, copper, mercury, and silver to the metallic condition. With molybdenum the reduction with these metals proceeds quite rapidly, but the speed diminishes with rise in atomic mass, so that the sluggish action of tungsten in ferric salts is not surprising.

THE DETERMINATION OF SULPHUR IN PYRITES.

A REPLY TO DR. LUNGE.

By Thomas S. Gladding.

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IN this Journal (June *1894*) I published an investigation of the several methods of estimating sulphur in pyrites. As a result of that investigation I rejected all other methods and recommended, in the strongest terms, the general scheme published by Dr. Lunge in his "Alkali-makers' Handbook." At the same time I advised a few minor modifications as conducive to greater certainty and accuracy. In this Journal (March *1895*) Dr. Lunge makes a vigorous attack upon each and every one of these modifications. An examination of his paper brings out the important fact that he admits that every modification proposed is accurate in its nature with one single exception. Unfortunately for Dr. Lunge, the single feature selected for condemnation is the one most easily capable of rigid and positive proof as to its absolute accuracy. I shall reserve the consideration of this point and take up in order the modifications to which such strenuous objection is made.

He objects to the use of one gram instead of half a gram. In reply I have found that by my method one gram is as easily handled as one-half gram and double the accuracy is attained in consequence. He objects to the use of a bromine solution instead of aqua regia as a solvent for pyrites. This substitution was made for the reason that quite often when using aqua regia I was annoyed by the separation of free sulphur. Since adopting the bromine solution I have *never* experienced this trouble.

His first important objection is against my direction to *always* dissolve the ferric hydroxide and test the same for sulphur. He declares that such procedure is unnecessary. On reading his comments on this point, however, we find that he admits that students in his own laboratory have sometimes failed to get out all the sulphur, through imperfect washing. He further "grants that in important cases the ferric hydroxide ought to be tested in some way or another for any sulphur left behind." If the washing out of *all* the sulphur is so absolutely certain as he claims elsewhere, why, it may be asked, does he grant what he does? The concession which he makes is a confession of uneasiness of mind on this very point and is all that I could ask for to justify my own instructions. In answer to his criticisms I will simply state that my washing of the precipitated hydroxide was made exactly as he directs. Five or six washings with hot water, "thoroughly churning" up the precipitate each time has never yet, in my hands nor in those of our assistants, completely removed all the sulphur when using one gram. When using one-half gram the danger of losing sulphur would undoubtedly be much lessened, but no careful analyst will neglect the very simple precaution of dissolving the ferric hydroxide in dilute hydrochloric acid and adding ten cc. of barium chloride to the filtrate.

Lunge's second objection is to my addition of the barium chloride solution, one drop per second, to the boiling sulphate solution. He admits that this method is entirely accurate but tedious and unnecessary, taking "about an hour." In reply I will first state that such addition requires only fifteen minutes, and as it is done automatically from a burette, requires no more labor than it does to "pour it in all at once."

But still further I condemn, as inaccurate, Lunge's method of adding the barium chloride all at once. The following comparative tests made, in part, by our assistant Mr. H. E. Cutts and, in part, by myself personally, are very conclusive on this point. A number of samples of pyrites were treated exactly alike in every respect except in the method of adding the barium chloride.

By slow addition. Per cent.	By sudden addition. Per cent.
50.23	50.84
51.00	51.20
51.00	51.32
51.20	51.50
39.13	39.35
39.40	39.90

In the last three samples the filtrates from the ferric hydroxide were divided into two equal portions, and one portion treated in the first manner, the other in the second. Still further tests were made by dissolving two and seven-tenths grams of chemically pure potassium sulphate in 400 cc. of water, adding five cc. of hydrochloric acid and treating as above.

By slow addition.		By sudden addition.
0.4960		0.4990
0.4960	Theory 0.4965	0.5020
		0.5021

I have also taken two grams of chemically pure ammonium sulphate, thus imitating more exactly the conditions of the pyrites analysis as carried out by Lunge and obtained

By slow addition.			By sudden addition.
0.4838	gram	sulphur	0.4868
0.4828	"	"	0.4900
0.4834	"	"	0.4888

Theory calls for 0.4848. The sudden addition of the barium chloride invariably gives results too high.

I quote the following private communication from Prof. Richards, of Harvard College, on this point. "I am much surprised to find that Lunge is ignorant of the occlusion of barium chloride by barium sulphate. This has been known for a number of decades. In 1890 it was so well known to me that I treated it as a matter of course (Amer. Acad. Proc., **26**, 258). This year one of my students has finished a comprehensive work upon this subject showing the amount and circumstances of the occlusion. The paper has already gone to press in the Proceedings of the American Academy and the *Ztschr. anorg. Chem.* It wholly confirms your unpublished statements made to Lunge." This is strong testimony corroborating my results given above. My method of avoiding the occlusion of barium chloride by adding the barium chloride solution *drop by drop* and thus insuring the formation of a chemically pure granular precipitate of barium sulphate is the same as that adopted by our National Association of Agricultural Chemists in the precipitation of phosphoric acid as ammonium magnesium phosphate.

The last objection of Lunge refers to my method of estimating the 0.20 to 0.40 per cent. of sulphur that may be left in the ferric hydroxide, by the simple plan of dissolving the latter in dilute hot hydrochloric acid, adding ten cc. of barium chloride solution and letting stand over night. This he declares is decidedly *wrong*.

Here again I will quote from Prof. Richards' letter. "This last paper (Dr. Lunge's) seems to me to contain several errors. I think you will find that *in the presence of a considerable excess of barium chloride*, barium sulphate is *not* very seriously soluble in cold ferric chloride solutions, even when acid (see Jannasch and Richards, *J. prakt. Chem.*, **39**, 328-329). Hence your method is as accurate as most analytical methods.

I wish to call especial attention to the method that Lunge has adopted to support his position on this point. He has taken four samples of pyrites and carried them through a complete analysis by his scheme and also by mine and because his method gives 0.20 per cent. more than mine he concludes that I lose 0.20 per cent. sulphur by the solubility of the barium sulphate in the acid solution of the ferric hydroxide. No such conclusion can be fairly drawn from so unscientific a procedure. A far better plan is to divest the problem of all other possibly interfering errors and strip it down to the naked question in hand. This had been done in my first paper as follows:

The insolubility of barium sulphate in the solution of ferric chloride thus obtained was demonstrated by dissolving 0.027 gram potassium sulphate in fifty cc. water, adding five cc. hydrochloric acid and 0.5 gram iron, precipitating hot and allowing to stand over night. We found:

1.	Sulphur	0.0049 gram.
2.	"	0.0050 "
3.	"	0.0051 "

The amount actually present was 0.00496 gram.

I have since repeated the above demonstration by an even more rigid test as follows: I dissolved 0.0135 gram of potassium sulphate in 100 cc. of water, added ten cc. of concentrated hydrochloric acid, one-half gram of iron, ten cc. of barium chloride solution, precipitating hot and allowing to stand as above. The barium sulphate came down slowly, on cooling. The ignited barium sulphate was snow-white and free from iron, probably on account of its slow formation; I obtained:

1.	Sulphur	0.0025
2.	"	0.0026

The amount actually present was 0.00248.

This amount taken in these last experiments corresponds to about 0.20 per cent. sulphur calculated on one gram of pyrites. Lunge claims to have lost this amount on account of the solubility of barium sulphate in acid solution. Were he correct I should have had no precipitate whatever in my experiments above. On the contrary I obtained the whole of the sulphur present to the one-hundredth of a per cent.

To determine sulphur in iron, Troilius, page 38, directs to "dissolve five grams in aqua regia, evaporate to dryness to make silica insoluble. To the filtrate from the silica, which should amount to at least 300 cc., a few cubic centimeters of barium chloride solution are added. After standing one night at the temperature of the room the barium sulphate is completely precipitated." Here we have ten times the amount of iron present that is contained in one gram of pyrites and yet no sulphur is lost. Had Lunge followed the safer and more scientific plan of testing this and also each of the other points in dispute, in the same way that I adopted in my original paper, namely, by working with known amounts of chemically pure salts containing known amounts of sulphur, he would not have fallen into the errors he has.

In conclusion: Of the main modifications proposed by me, Dr. Lunge admits that all are entirely correct, with one exception. The one which he claims to be inaccurate I have incontestably proven to be wholly right. I have also shown that the modification of adding barium chloride, drop by drop, is absolutely necessary to accurate results. I have also shown that the solution of the ferric hydroxide and testing the same for sulphur is certainly the safer course. I conscientiously advise my brother chemists to modify Lunge's method in accordance with my instructions.