obtained which agree very favorably with those obtained with pure copper sulphate solutions.

In No. 1 of the last method we used as the dissolving solution, a solution of 2.5 grams ferric chloride, 25 cc. distilled water and 3 cc. sulphuric acid, but before titrating added 20 cc. of titrating mixture. In No. 2 the ferric chloride was replaced by ferric sulphate, but no titrating mixture was used. In making the computations the iron factor was multiplied by 1.138 to give the copper value. Recalculating the results, using the factor 1.092, we obtain 33.90 per cent. and 32.84 per cent., or an average of 33.37 per cent. copper,—a result which approximates the results obtained by the other methods.

In nearly all of the above methods, the determinations were carried out by each of us independently. In this way the weak points of the methods were brought out more clearly, and gave us a check on our work.

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THE CAUSTIC SODA METHOD OF DETERMINING MOLYBDENUM IN STEEL.[1]

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THIS method as described by the writer in the *Iron Age*, November 20, 1902, was taken up by Cruger and Miller,[2] tested by them and compared with a method of their own which they suggest and describe, and which differs from the writer's method in that the iron is separated from the molybdenum by hydrogen sulphide instead of by caustic soda. The conclusion that their experiments bring them to is that the caustic soda method gives results that are about 0.30 per cent. too high in steels, and about 2.00 per cent. too high in ferromolybdenums, on account of the formation of a molybdate of iron soluble in caustic soda or ammonia. It seemed to the writer that this conclusion was based on insufficient evidence. It is true that the fact that in their experiments, the caustic soda results are lower than results by their own method as above stated is a

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[1] Read at the June Meeting of the Philadelphia Section of the American Chemical Society.

[2] This Journal, **26**, 675.

very significant one, when taken in connection with the other fact that their method always brings good results when tested against standard methods—and they make many such tests. And when in addition to these experiments, the authors test the caustic soda solution of the molybdenum after filtration from the iron, qualitatively with potassium thiocyanate, and find iron present, the evidence in favor of their conclusion would seem to be so strong, that it would hardly occur to one to question its correctness, were it not for a quantitative test that they also make (but to which strangely enough they seem to attach no significance), which not only does not corroborate their opinion that the high results by the caustic soda method are due to some iron going into solution in the caustic soda as a soluble iron molybdate, but absolutely disproves that opinion, and indicates that the iron is simply due to traces mechanically carried through the filter-paper by the strong caustic soda. This experiment was as follows: An iron and molybdenum solution was made up in something like the proportions existing in a ferro-molybdenum, the molybdenum separated from the iron by caustic soda, and the latter then tested quantitatively for iron, after getting rid of the molybdenum with sulphuretted hydrogen. Now, to corroborate their theory that the 2.00 per cent. too high molybdenum results, are due to iron dissolved in the caustic soda as iron molybdate, they should have found in this experiment about 0.0200 gram iron oxide. The amount actually found was only 0.0005 gram, or enough only to make a difference of about 0.05 per cent. in the molybdenum result instead of 2.00 per cent. This result would indicate that the iron found by their qualitative tests with sulphocyanide was simply very minute amounts carried mechanically through the filter-paper by the strong caustic soda. This is something the writer for his part, had always been suspicious of and has habitually used double filters, and moreover carried on the dummy test on drillings of molybdenum-free steel instead of on the reagents simply. Evidently, more work is needed before Cruger and Miller's conclusions can be accepted as proved, and the writer resolved to investigate the point thoroughly. It would seem that the question that results by the caustic soda method are too high (0.30 per cent. in steel, 2.00 per cent. in ferro-molybdenum) by reason of a soluble iron molybdate, could best and easiest be investigated and settled as follows: Let such weights of ordinary C. P. molybdic acid and of steel drillings free from molybdenum be taken as would together correspond to 0.8 gram of a molybdenum steel, or of a ferro-molybdenum. Ordinary C. P. molybdic acid is, of course, far from pure, but for the purposes of this investigation this does not matter. Nor is it in the least necessary to determine the amount of molybdenum in the molybdic acid used. Then let the molybdenum in this mixture be determined by the caustic soda method, as usual. Then let precisely the same weight of molybdenum trioxide be taken for a second experiment, in which the drillings are omitted, carrying out the caustic soda process on the molybdenum trioxide alone, using the same measuring flasks as were used in the first experiment. Now, if the result in the first experiment (when the drilling is used) comes notably higher than the result by the second experiment (when the molybdenum trioxide alone is used), and if at the same time, a quantitative test in the first experiment shows about 0.0030 gram iron oxide (or 0.0200 gram if the proportions be those of a ferro-molybdenum) in the caustic soda solution along with the molybdenum, then, of course, it is proved that Cruger and Miller are right, and a molybdate of iron soluble in caustic soda makes the molybdenum results by this method too high. But on the other hand, if results by these two experiments agree, and if no iron oxide is found with the molybdenum in solution in the caustic soda, then Cruger and Miller must be in error.

The following tests were made by the writer:

No.	MoO_3 and drillings. Molybdenum, per cent.		MoO_3 alone. Molybdenum, per cent.	
1	8.75	8.695	8.67	8.61
2	8.67		8.50	
3	8.67		8.67	
4	43.25		43.35	

These results do not at all bear out Cruger and Miller's contention. It is seen from the above table that results come no higher than when there is no iron at all present. But although these results do not corroborate Cruger and Miller's theory of a soluble molybdate of iron, still, on the other hand, they cannot be taken as absolutely disproving it, for it is not impossible that some other error might counteract and mask the effect of the soluble iron molybdate. For instance, there may have been a loss of molybdenum through some of it coming down with the ferric hydroxide precipitate, or there may have been enough iron present as an impurity in the C. P. molybdenum trioxide used in the experiments, to form the same amount of soluble iron molybdate. To conclusively prove or disprove the point, it is obviously necessary to make a quantitative determination of the iron in the caustic soda solution of the molybdenum, after the separation from the bulk of the iron by the caustic soda. The following test was thereupon made. Molybdenum trioxide, and steel drillings in the proportions of a molybdenum steel were mixed, dissolved, and the caustic soda separation made as in the regular method. Then instead of finishing as usual, by reducing with zinc and titrating with permanganate, the caustic soda solution of the molybdenum was quantitatively tested for iron as follows. After strongly acidifying with sulphuric acid, the molybdenum was precipitated by hydrogen sulphide, filtered off, redissolved and reprecipitated, and the combined filtrates from the molybdenum sulphide again precipitated with hydrogen sulphide, and filtered from the molybdenum sulphide washed through in the first operation. The hydrogen sulphide was then boiled off, the solution oxidized by nitric acid, evaporated, the silica separated and the iron precipitated with ammonia. With the iron is precipitated the alumina derived from the caustic soda originally used and from the glass vessels. To free the iron from this, the ignited precipitate was fused with a large excess of sodium carbonate, dissolved in water, filtered, dissolved in acid, precipitated with ammonia, and again fused with sodium carbonate, etc., and a third fusion made, and the iron finally precipitated with ammonia.

From the very start a blank or dummy test was, of course, carried along with the regular test. The iron oxide finally weighed was found to have exactly the same weight in the regular test as in the blank or dummy test, showing that no iron whatever had gone into the caustic soda solution as a soluble iron molybdate, and disproving Cruger and Miller's theory. According to them, about 0.0030 gram of ferric oxide should have been found in this experiment. Actually not a trace was found as just stated. Not satisfied with this experiment, another was made in a sample made up to correspond to ferro-molybdenum in the proportions of iron and molybdenum present. In this last experiment 0.0200 gram iron oxide should have been found if Cruger and Miller's theory is correct. But as in the first experiment, not a trace was found, the regular test, and the blank or dummy test weighing exactly the same. The question now arises, since the soluble iron molybdate theory proves to be untrue, what then is the real reason that Cruger and Miller obtain so much higher results by the caustic soda method than by their own method, which differs from it only in that the iron is separated from the molybdenum by hydrogen sulphide instead of by caustic soda? Assuming their method to be an accurate one, why does the caustic soda separation of iron from molybdenum give too high results? Or, on the other hand, if the caustic soda separation is accurate, why does the hydrogen sulphide separation give too low results?

To the first of these questions it would be difficult to find an answer, now that the soluble iron molybdate theory has been found inapplicable, but to the second an answer readily suggests itself. It is, that the reason why the hydrogen sulphide separation gives too low results is because some of the molybdenum sulphide is lost in the washing, as, according to the writer's experience, is the case with copper and nickel sulphides. But to this theory the objection at once arises that Cruger and Miller thoroughly tested the accuracy of this method in a long series of experiments, in which results by their method agree well with results by the lead molybdate method of Chatard, and by the electrolytic method of Smith and Kollock. But to this objection also a reply may be found. Cruger and Miller standardized their permanganate solution by ferrous ammonium sulphate, and again with oxalic acid. Now, it is the writer's experience with the former of these two reagents, that it sometimes happens that the salt does not contain the full amount of ferrous oxide, and the permanganate solution standardized against it, therefore, in such cases is given too high a strength. With oxalic acid the writer has never had any experience, but it is perhaps not impossible that it also is sometimes not pure, and if so, and if also Cruger and Miller had the bad luck to strike faulty samples of both these substances, then it is at once seen how their molybdenum results could come too high by the caustic soda method, and at the same time about right by their hydrogen sulphide method. The results by the caustic soda method would be too high because the strength of the permanganate used in the method was too high, and the hydrogen sulphide method results would be correct because the error from the use of the same permanganate is counterbalanced by the loss of molybdenum in washing the sulphide. To this it will be objected that Cruger and Miller get high results by the caustic soda method even when they finish as lead molybdate, instead of titrating with permanganate. But here again an explanation is possible, which is that weighing as lead molybdate after the caustic soda separation, would also bring too high results, on account of contamination with alkali or alumina from the large amount of caustic soda used. A blank or dummy test would, of course, prevent error from alumina, if not too strongly acid with acetic acid, but not from alkali.

At any rate, it would seem to be not an unreasonable opinion that the method of Cruger and Miller is not yet placed above suspicion, and it is to be hoped that the authors will put more work on it. The writer also hopes to find opportunity to test the hydrogen sulphide separation himself, but in the meantime must disbelieve that the caustic soda method gives too high results, either by reason of a soluble iron molybdate, or for any other reason.

But the writer has found it advisable to slightly modify the manipulation as described by him in the *Iron Age*,[1] and the process now used is as follows: An 0.8 gram factor-weight is dissolved in nitric acid (also for a blank or dummy test, the same weight of some molybdenum-free steel, if the caustic soda solution is a new one), evaporated to dryness, boiled with 25 cc. strong hydrochloric acid, and evaporated to fumes with 10 cc. dilute (3:1) sulphuric acid. Taken up with 50 cc. water, and poured gradually and with shaking into 100 cc. caustic soda solution (1 pound to 2100 cc. water) contained in an 8-oz. Erlenmeyer flask provided with a file mark at 200 cc., then diluted to the mark, mixed, and 100 cc. taken of filtrate, acidified with 15 cc. strong sulphuric acid, reduced with zinc, and titrated with permanganate.

Vanadium, if present, would be reduced by the evaporation with strong hydrochloric acid, and if it then all goes into solution in the caustic soda along with the molybdenum (as seems to be the case), then the method of Glasmann[2] would seem to be the proper plan, although the writer has not yet tested it. This method determines the vanadium by reducing with zinc to the V_2O_2 form, and

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[1] November 20, 1902.

[2] *Ber.*. **38**, 600.

titrating with permanganate, then in another test reducing with magnesium to the V_2O_3 form, and titrating, the difference between the two titrations showing the permanganate required to oxidize the V_2O_2 to V_2O_3. Tungsten, if present, must of course first be separated in the usual way by evaporation of the hydrochloric acid solution. But the tungsten trioxide thus obtained has a great tendency to carry down other oxides as iron, chromium and it would also seem, molybdenum; and just as the iron and chromium contamination of the tungsten trioxide must be allowed for (it is not necessary to determine this contamination in every case) so, of course, we must find and apply the correction for the molybdenum carried down with the tungsten, not for use in the tungsten determination, as there the molybdenum would volatilize in the ignition, but for use in the molybdenum test. The easiest way of determining the proportion of molybdenum carried down with various weights of tungsten trioxide, is, not to attempt a separation of the two, but to add a known amount of pure molybdenum trioxide to tungsten steels (free from molybdenum) and see how much of the molybdenum found by analysis falls short of the amount originally added; or, what amounts to the same thing, to compare results obtained in this way, using ordinary C. P. molybdenum trioxide with results obtained from the same amount of the same trioxide added to steel free from tungsten (and of course molybdenum). The following results were obtained:

No.	Tungsten. Per cent.	Molybdenum added. Per cent.	Molybdenum found. Per cent.
8661	17.57	8.67	8.75
8544	8.63	8.67	8.42
8542	9.64	8.67	8.58
8551	5.24	8.67	8.42

The greatest loss is 0.25 per cent., from which it is seen that a correction of 0.13, or half this amount, would be about the right one to employ in all cases.

In actual practice it is rare to find molybdenum and tungsten in the same steel (the writer has never had a case) for the reason that molybdenum is used as a substitute for tungsten in high speed tool steels, etc., and therefore when it is used, the tungsten is dispensed with usually.

LABORATORY OF HENRY DISSTON & SONS' STEEL WORKS.