method of sufficient rapidity that suits our needs better or with which we can get better results, when proper precautions are taken, than the molybdate method.

It may be of interest here to give also a brief summary of the results on these same phosphate solutions by the volumetric method as investigated this year. The results were obtained by some of the same chemists who analyzed these samples by the gravimetric method. This was the first time the volumetric method in its present form had been used by most of them.

Thirteen chemists reported thirty-one determinations on solution No. 1 and thirty-three on No. 2 by the volumetric method. Seventy-three per cent. of all the results on No. 1 were within 0.05 per cent. of the theory, and ninety-three per cent. were within one-tenth per cent., there being only three results varying more than one-tenth. On sample No. 2 eighty-five per cent. of the results were within 0.05 per cent. of the theory, and all were within one-tenth.

The results upon which the foregoing discussion is based will appear in the proceedings of the A. O. A. C. in the "Report on Phosphoric Acid," made by the writer to that association at its recent meeting.

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THE VOLUMETRIC ESTIMATION OF MANGANESE.

BY GEORGE AUCHY.

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IN this Journal, **17,** 5, Mr. W. H. Thomas describes his experience with Low's and with Volhard's method of determining manganese. The latter he finds reasonably accurate. The former not at all so. Some ten or twelve years ago, in the transactions of the American Institute of Mining Engineers, Williams' method in steel, which is based on the same principle as Low's method in ores, was the subject of considerable controversy; some claiming, others disputing its accuracy. And although the weight of the testimony seemed to be in favor of the method, nevertheless, the close of the discussion left the matter still somewhat in doubt.

Are methods based upon this principle reliable? Mr. Thomas' experience with Low's method is further evidence to the contrary. But as regards Williams' method, perhaps it may be said that Mr. Thomas' results are not in evidence, inasmuch as potassium chlorate and strong nitric acid are stronger oxidizing agents than bromine water, and may therefore be depended upon to oxidize the manganese completely to manganese dioxide, even if the latter cannot be. But Mr. Stone's and others work is against this assumption; also the following results obtained from manganese ores:

	Williams' method (practically) per cent.	Volhard's method. per cent.
Ore No. 1	51.71	53.04
" " 2	51.58	53.00
" " 3	44.88	46.80
" " 4	43.00	46.24
" " 5	41.22	42.64
" " 6	34.39	40.00
" " 7	44.88	46.40
" " 8	31.61	43.76

Among steel works chemists, Williams' method is very popular on account of its great ease and simplicity. Comparatively few, perhaps, use Volhard's method. And it is therefore important that the reliability of the former method be more fully and definitely established. So far, the evidence in its favor is strong and positive. But there is still room for doubt. More work seems to be required to fully settle the question, and it would be well for chemists who use this method, to patiently check with Volhard's method for a considerable time, (using different lots of chlorate) and communicate their results and opinions to the Society. I say Volhard's method, because the gravimetric is too cumbersome for such an extended use, and is probably moreover not any more accurate—perhaps not so much so—as Volhard's.

My own experience with Williams' method leads me to believe that it usually, but not always, gives accurate results. And I am disposed to think that if chemists who have repeatedly obtained good results with that method, and who have therefore every confidence in it, would nevertheless keep on for an extended period checking their results by Volhard's method they would sooner or later be treated to a disagreeable surprise such as illustrated by the last four of the following results :

		Williams' method. per cent.	Volhard's method. per cent.
Heat	114	0.42	0.42
Rolled steel	...	0.43	0.45
Heat	116	0.50	0.50
"	120	0.40	0.41
"	121	0.42	0.42
Tire steel	...	0.92	0.94
Heat	125	0.48	0.54
Tire	...	1.04	1.20
Heat	162	0.37 and 0.42	0.45
"	163	0.40	0.48

With heat 163 Williams' method was given up.

With regard to the method of oxidizing to permanganate by lead oxid and titrating with arsenious solution, without having given the method actual trial, I am nevertheless convinced that it gives uniformly low results, from the fact that while it was in use at these works, 135 and 140 pounds of ferromanganese per charge was needed to bring the manganese content to the required point, working by this method, while now, with Volhard's method in use, only ninety and 100 pounds are used to bring the same result. But the lead oxid used in the method was the tetroxide. Probably by the use of dioxide, good results may be obtained.

For the benefit of chemists, who have never used Volhard's method, and who feel disposed to give it a trial, for the purpose I have suggested, I beg to call attention to certain precautions which are essential to a successful practice of the method.

1. In boiling off the nitric acid with sulphuric acid, it is very essential to avoid too much sulphuric acid, as otherwise the bumping and spattering will be so violent as to altogether spoil the test.

2. The dry mass should be taken up with *hot* water, allowing the dish first only a minute or two for cooling. If the dish be allowed to cool completely, and cold water be added, and then boiled up, very frequently a red ferric sulphate carrying much manganese will remain insoluble, no matter how much additional sulphuric acid be added. Even this precaution is value-

less, however, if the dry mass be heated too long. But this residue can be brought into solution by decanting the clear solution and then heating for some time with sulphuric acid. But to save time its separation should of course be prevented in the first place.

3. In steels high in manganese it is advisable, and in steels low in manganese it is absolutely essential that not too much zinc oxide be used; as it will separate out when the solution is heated, if much has been used, and will retard the settling of the manganese dioxide if the steel be high in manganese, and will completely prevent it if the steel be low in manganese, (0.18—0.24 per cent.) and thus make the observation of the end of the titration impossible. Before the zinc oxide is added, therefore, the solution should be in as small a bulk as convenient and be as nearly neutralized with sodium carbonate as possible.

4. When titrating with permanganate, the reddish color caused by the permanganate should be completely changed into clear yellow by shaking the flask before more permanganate is added, and at the end the liquid must be distinctly and permanently rose colored—that is, it must retain its color through a dozen good shakings. It is well, toward the end, to add the permanganate four drops at a time (when two drops equal one-tenth cc.) till the distinct rose-tint is reached, and then deduct one-tenth cc. from the reading of the scale.

It may be a convenience to state the method in detail. Take exactly three and three-tenths grams in a six-inch evaporating dish. Cover and dissolve on the hot plate in forty cc. of nitric acid containing a little more than half of strong acid. Add eight cc. (no more) strong sulphuric acid. If, however, the liquid becomes cloudy on boiling, the violent bumping and spattering before referred to will inevitably occur as the boiling progresses further. Add then at once some strong hydrochloric acid, and transfer to a wire gauze, where boil down rapidly over a good strong flame till the mass is nearly dry—a little pastiness still remaining here and there. It is best to remove the cover when the liquid gets pasty. Allow to cool a minute or two. Take up with hot water and boil a few minutes. Cool by placing in a larger dish of cold water. Pour into a 500 cc. measuring flask. Nearly neutralize with sodium carbonate. Add zinc oxide emulsion until sudden stiffening of the solution. Dilute to the mark. Pour in a dry beaker, mix with rod, and pour through a very large ribbed filter into a 250 cc. measuring flask. When the liquid has reached the mark, withdraw, and transfer to a 500 cc. Erlenmeyer flask. Heat to boiling. Add nearly the full amount of permanganate of strength exactly 0.0055, if the percentage of manganese is approximately known. If not add only one and a half cc. permanganate, and boil until the manganese dioxide separates in flakes, and the liquid becomes yellow. Finish the titration shaking after each addition of permanganate till the yellow reappears. The number of cc. permanganate divided by ten will give the percentage of manganese.

Where the method is in daily use, it will be well to use for neutralizing before adding zinc oxide common sal soda instead of the expensive chemically pure carbonate. But this will add about 0.03 per cent. to the manganese, and must be determined and deducted. The sal soda can be procured at grocery or drug stores. Two pounds in two liters of water (and filtered) is a convenient solution.

The impurity is best determined by doing a steel with pure sodium carbonate, then with the sal soda. For convenience, the amount of the soda solution required to nearly neutralize the manganese solution is noted, and that amount is then at once added in subsequent determinations.

AN EARLY AMERICAN ARRANGEMENT OF THE ELEMENTS.

BY F. P. VENABLE.

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IN going over the papers published during the period immediately following the announcement of the Periodic Law, there is one which possesses especial interest for an American.

It is the "Synoptical Tables of the Elements" by Dr. L. R. Gibbes, of Charleston, appearing in the publications of the Elliott Society in 1875. This table had been prepared some two or three years previously for the use of his classes. In it a professor in a remote and small American college worked out for himself, evidently in ignorance of the arrangements of Mende-