

dissolved in 6 to 10 cc. of water, and this solution used for the analysis. The portion to be tested for calcium may be treated with a drop of ammonium hydroxide solution to insure the absence of free acid.

In the use of the above method, particular attention should be given to the following points: The potassium iodate solution used as a reagent must be fully saturated. This reagent is conveniently prepared by using enough of the dry salt to make a $N/2$ solution and allowing it to stand some hours, with occasional shaking. If it is desired to dissolve the salt more quickly by heating to boiling, the warm solution must be cooled to ordinary temperature and agitated before use.

In adding the reagents, particularly the iodate and hydrochloric acid solutions, the amounts added must correspond quite closely with what is called for in the directions given above. The adequacy of these directions has been tested by their employment in analyses of some forty mixtures by myself and others, in the laboratory of the University of Cincinnati. The results obtained were entirely correct.

I desire to express my sincere thanks to Dr. J. F. Snell, whose continued encouragement and suggestions have been invaluable, in this, as in my previously published work.

THE DETERMINATION OF TOTAL ARSENIC ACID IN LONDON PURPLE.

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MOST methods now in use for the determination of arsenic acid, present, when applied to London purple, certain serious difficulties, to avoid which was the object of the work outlined in the present paper. The Association of Official Agricultural Chemists recommends the method stated briefly as follows:¹

Two grams of the sample are dissolved in 80 cc. of water and 20 cc. of hydrochloric acid at about 70° , one-sixth of this solution is treated with 50 cc. of hydrochloric acid and 3 grams of potassium iodide and allowed to stand, by which means all of the arsenic is reduced to the state of arsenious acid. The free iodine is removed by the addition of $N/10$ sodium thiosulphate; the

¹ U. S. Dept. Agr., Bur. Chem., Cir. 10, p. 4.

solution is now made alkaline with solid sodium carbonate, the excess of this removed by means of hydrochloric acid, and then sufficient solid sodium bicarbonate added to make the solution decidedly alkaline. The solution is then titrated with standard iodine solution. Total arsenious acid having been determined in a similar manner, omitting the reduction by hydriodic acid, the total arsenic acid is calculated by difference.

The presence of the large amount of purple dye which is always found in London purple is not particularly objectionable to the practiced operator when titrating in basic solution with iodine, but in strongly acid solution, such as is present during the reduction of arsenic acid, it becomes practically impossible to determine when the iodine, liberated by the action of arsenic acid upon hydriodic acid, is exactly used up by the sodium thiosulphate, even by the use of the outside testing method recommended by the association. Davidson¹ directs that a part of the dye be precipitated by the addition of sodium carbonate, the solution filtered and an aliquot portion be treated with hydrochloric acid and potassium iodide. This is certainly an improvement but is, in the opinion of the writer, far from being a completely satisfactory method, inasmuch as a considerable portion of the dye remains in solution, even after this treatment.

Since the arsenic is eventually all brought to the lower state of oxidation and any intermediate oxidation or reduction should occasion no error in the determination, it seemed possible that the solution might be successfully bleached by chlorine and all interfering dye destroyed. This point was investigated, with results which will appear later.

The neutralization of a considerable amount of hydrochloric acid by means of powdered sodium carbonate is a quite tedious operation in this case, not only on account of the tendency of the carbonate to form lumps in the solution, these acting only slowly upon the acid, but also because an excess of sodium carbonate must be avoided on account of the later use of iodine. Since the acid becomes very dilute toward the last, the action becomes correspondingly slow from this cause. The formation of lumps may be partially avoided by the use of the crystalline form of sodium carbonate, but in any case the slow addition of a rather large quantity is necessary and the bicarbonate must be added later.

¹ U. S. Dept. Agr., Bur. Chem., Bull. 99, p. 27.

It was thought possible that the amount of acid used, consequently the amount of carbonate required, was unnecessarily large in both methods, also that a calculated amount of sodium bicarbonate might be substituted for the normal carbonate, adding the former as rapidly as could be done without danger of loss by frothing, in this way providing a large surface for the action of the acid when the latter becomes dilute.

Experimental work was undertaken in order to determine the measure of accuracy of a method involving the changes suggested above, with results which follow.

Chlorine, evolved by the action of potassium permanganate upon concentrated hydrochloric acid, and passed into the warm semi-solution of London purple in hydrochloric acid, produces in less than ten minutes a brown precipitate of organic matter which, after removal by filtration, leaves a slightly yellow solution in which the titration of iodine with sodium thiosulphate and of arsenic with iodine is easily accomplished. The presence of chlorine in the solution and the fact that all of the arsenic is in the oxidized form necessitate, of course, the presence of a somewhat larger quantity of potassium iodide.

The amount of acid added to the aliquot part of the solution in which the arsenic acid is to be reduced was changed from the 50 cc. of the official method or the 25 cc. of Davidson's modification, to 10 cc. The reduction of arsenic acid is, as might be expected, not complete at the moment of the addition of hydrochloric acid and potassium iodide, nor does this reduction proceed as rapidly during the addition of sodium thiosulphate as is the case with larger amounts of acid, but it was found that the reaction was sufficiently rapid to serve the purpose and, since one of the products (iodine) is removed to practical completion, the reaction is quantitative.

Powdered sodium bicarbonate was substituted for the normal carbonate, using a weight calculated to leave an excess of from 3 to 5 grams after the neutralization of all of the acid. Although this causes a more copious evolution of carbon dioxide, it was found possible to complete the addition in less time than was the case with the normal carbonate, for reasons already mentioned.

The method finally used for total arsenic acid is as follows: Warm 4 grams of London purple, 40 cc. of concentrated hydrochloric acid, and 150 cc. of water to not over 80° in a 250 cc.

flask, until the soluble portion has dissolved. Immediately pass in a rapid stream of chlorine for ten minutes; transfer to a 500 cc. graduated flask, dilute to the mark with cold water, and mix. Filter through a folded filter, rejecting the first 30 to 50 cc. Measure 50 cc. of the nearly colorless solution into a 500 cc. Erlenmeyer flask, add 10 cc. of concentrated hydrochloric acid and warm to 80° on the water-bath, then add 5 grams of potassium iodide and allow to stand for ten minutes. At the end of this period add sodium thiosulphate (about N/20) from a burette until the iodine is exactly removed. It is best to avoid the addition of starch solution at this point, on account of the deep red color which is produced by the action of iodine upon dextrin, the latter being almost invariably present or formed in strongly acid solutions of starch. Immediately add, as rapidly as can be done without loss by effervescence, 15 grams of sodium bicarbonate, free from lumps, using a drop of methyl orange to insure the final presence of a decidedly basic solution. Titrate at once with N/20 iodine solution, deferring the addition of starch as long as possible.

Determine the total arsenious acid by either the official method or Davidson's modification, and subtract the percentage found from that indicated by the above titration. This gives total arsenic acid.

The use of chlorine gas may constitute with some operators an objection to this method, but if a good draught hood is available, this objection becomes of small importance. Chlorine is best generated, for this purpose, by dropping pure concentrated hydrochloric acid from a dropping funnel upon pure potassium permanganate contained in a flask, as this yields a fairly constant and easily controlled stream of gas, free from arsenic. The gas need not be washed.

Samples of London purple, analyzed by this method, gave results agreeing well with those obtained by the official methods, and duplicate determinations may be made to agree with each other to within a few hundredths of a per cent. The time consumed in making a determination is materially shortened and the difficulties of manipulation are decidedly decreased. Moreover, students using the method for the first time experience little trouble in obtaining accurate results, and this was never accomplished when any other method was used.