

ART. XXV.—*The Volumetric Determination of Small Amounts of Arsenic*; by LAUNCELOT W. ANDREWS and HENRY V. FARR.

THE problem of the analytical determination of small amounts of arsenic, present as an impurity in products of the most varied character, is a constantly recurring one. The comparison of mirrors formed in the Marsh test in its several modifications and a few colorimetric processes have solved the problem for the special case in which the arsenic is present in traces only and in which a merely approximate estimation of the amount suffices. We have been led to seek a solution covering a wider range of cases, in which, for example, the arsenic may be present in any quantity from 0.1 mg., or possibly less, to 100 mg. and in which the accuracy of an ordinary quantitative analysis is required.

Often, but not always, the distillation of the arsenic, after Fischer as arsenious chloride, furnishes satisfactory results under these conditions as a method of separation, but it always has the disadvantage of being rather time-consuming. It is better adapted for the determination of larger than for smaller amounts, since the distillate contains its arsenic in a highly dilute state and much contaminated with foreign salts,* or else in the form of arsenic acid,† which is not particularly well suited to quantitative determination. A method, in order to be perfectly satisfactory for the purpose in view, should comprise: (A) a process for the direct separation of the arsenic in a concentrated form, applicable to the greatest possible number of cases; (B) a simple, rapid procedure for determining the arsenic in the form in which it is furnished by step (A).

It is obvious that none of the existing methods can meet these demands. The well-known Bettendorff test,‡ in which the arsenic is precipitated in the metallic state by a mixture of hydrochloric acid and stannous chloride, appeared to us to possess possibilities of development for the process we were looking for. This test has been used by E. S. Peck§ for the colorimetric determination of arsenic in metallic iron. According to Bettendorff (l. c.) the sensitiveness of the reaction is such that it will show "most definitely" the presence, in one cubic centimeter, of two millionths of a milligram of ammonium-magnesium arsenate, that is, of less than a millionth milligram of metal. Our own observations on this point con-

* Alkali chloride, if the distillate is received in alkali hydroxide solution.

† When the distillate is received in nitric acid or other oxidizing agents.

‡ *Fres. Zeitschr.*, ix, 105, 1869.

§ *Pharm. Jour.* (4), xiii, 130, 1901.

firm the statement quoted, provided, naturally, that a layer of sufficient thickness be examined and that the liquid is otherwise absolutely colorless.

The arsenic as thrown down in the Bettendorff test, although finely divided, settles in two or three hours and can be filtered on the expiration of that time through an asbestos filter without exhibiting any tendency to run through, and can be washed with concentrated hydrochloric acid and with water, without undergoing oxidation. As pointed out by Bettendorff, it contains more or less tin. Bettendorff found 95.86 to 98.56 per cent of arsenic. The amount of tin, present as basic chlorides, varies, however, over a much wider range than these figures would indicate, depending on the amount of oxidation undergone by the stannous chloride, the temperature, etc. The precipitate dissolves in decinormal, centinormal, or millinormal iodine solution, made slightly alkaline by addition of suitable amounts of sodium bicarbonate or phosphate. The readiness with which this solution occurs depends mainly on the amount of stannic acid or of basic stannic chlorides carried down with the precipitate. If the degree of this contamination is considerable, the precipitate must be shaken for several hours with the liquid in order to effect complete solution; but if the amount be smaller or vanishing, solution takes place in less than a minute. This observation led us to prevent co-precipitation of basic tin compounds by adding tartaric acid to the reaction mixture of hydrochloric acid, stannous chloride and arsenite. There seems to be no inclination for the precipitate to entrain stannous compounds.

Bettendorff found the reaction to be incomplete, even after the lapse of a long time, with hydrochloric acid of 23 per cent HCl, while with such of 25 per cent it was complete "after some minutes." This concentration represents the minimum. It is better to operate with a concentration of nearly 30 per cent, which presents no difficulties when the ordinary reagent acid of 40 per cent is used. That is to say, 25^{cc} of the latter acid should be employed as a minimum to each 10^{cc} of the solution to be examined.* The most obvious cause of errors lies in the possibility of loss by evaporation of the highly volatile arsenious chloride during the reduction process. This we guarded against in our earliest experiments by sealing up the reaction mixture in glass tubes, an effective but inconvenient

* This rests of course on the assumption that the substance to be examined contains nothing to neutralize the hydrochloric acid. Otherwise a far greater amount of acid may become necessary. Thus when tartar emetic is to be examined for arsenic, the salt is dissolved directly in the 40 per cent acid, and enough of the latter must be taken to furnish 25 to 30 per cent of absolute acid, *after* that consumed in converting the potassium and the antimony into chlorides has been duly allowed for.

expedient, which fortunately proved to be unnecessary, since sufficient protection is afforded by closing the solution in a bottle with a well-ground glass stopper, provided the temperature is not raised higher than 35° or 40°. The latter should not be lower than 25°, since the reaction then becomes undesirably slow.

In the absence of tartaric acid, the arsenic does not usually visibly deposit on the glass walls, but when the precipitation of tin compounds is prevented, a small part of the arsenic sometimes forms an extremely thin film, adherent to the glass. The existence of such a film should be assumed, even when none is visible. Experiment has demonstrated that a minute truly, but titratable amount of arsenic may be present in this way on the seemingly quite clean surface of the vessel in which the reduction has taken place.

The process finally assumed the following form. The material to be examined, if in the form of a solution more bulky than 20^{cc}, is neutralized and boiled down to 10 or 20^{cc} and transferred to a white bottle of 80 to 100^{cc} capacity, provided with a very well-ground stopper. To the liquid is added two and a half times its volume of the tin reagent, prepared by dissolving twenty grams of stannous chloride crystals and forty grams of tartaric acid in one liter of forty per cent hydrochloric acid.* The stopper is inserted and the flask set aside to stand in a warm place till the precipitated arsenic has subsided, leaving the supernatant liquid water-white† and clear. This usually takes about two or three hours, more or less, if the temperature is nearly 40°. An asbestos filter is prepared in the usual manner, either in a Gooch crucible or in a Neuman filter tube. The precipitated arsenic is transferred to the filter with the aid of a small amount of concentrated hydrochloric acid, rigorously chlorine-free. The flask is rinsed repeatedly with small amounts of water which are passed through the filter, which is completely washed by aid of suction without allowing it to be exposed to the air more than necessary, except at the last draining, a precaution which may not be requisite, but which seems indicated. The proper amount of centinormal or of decinormal iodine solution is now measured into the flask by a pipette as indicated by the equation,



allowing for an excess of ten to one hundred per cent above

* This reagent will remain colorless if the constituents are arsenic-free. It should be kept in bottles holding not more than 200^{cc} and closed in such a manner as to give assurance of protection of the contents against oxidation.

† Of course this does not apply when nickel chloride or other colored salts are present.

the theoretical.* The precipitate, with the asbestos filter, is now transferred quantitatively to the flask and shaken with the iodine solution.† Enough of a five per cent solution of sodium bicarbonate or of sodium phosphate should now be added to maintain neutrality throughout the reaction, but not an unduly large excess, and the shaking be continued till the asbestos is thoroughly disseminated through the liquid and till it is certain that every particle of arsenic is dissolved. Fresh starch paste is added and the excess of iodine is titrated back by hundredth or thousandth normal arsenite solution.

For quantities of arsenic smaller than 0.5 mg., thousandth normal solutions may be employed, but it must not be forgotten that in such high dilutions a correction must be employed for the amount of iodine required to produce the end-reaction, if satisfactorily exact results are required. This correction usually amounts to about 0.6^{cc} of N/1000 for each 50^{cc} of solution, but it should be determined under the actual conditions of the titration. A main factor influencing the sensitiveness (aside from temperature) is the concentration of iodide in the liquid. For larger quantities than 10 mg. of arsenic up to 100 mg. tenth normal iodine solution is preferably employed.

The degree of precision to be expected in the results obtained by this method may be seen from the following test analyses. A hundredth normal arsenic solution (containing 0.375 mg. As per cc.) was made by dissolving 990.0 mg. of As₂O₃ in water to make two liters, and also a fifth normal

TABLE

	Arsenic taken Milli- grams	Volume of solution cc.	Vol. of HCl used cc.	Vol. of iodine sol. added	Vol. of As sol. req.	Weight of As found	Error mg.
1	3.75	10	25	50.02N/100	25.02N/100	3.75	0.00
2	3.75	10	25	41.05	16.03	3.753	+0.003
3‡	3.75	10	50	30.03	5.23	3.72	-0.03
4	7.519	20	60	60.06	10.00	7.510	-0.01
5	0.375	2	10	5.01	2.46	0.382	+0.007
6	71.02	10	30	51.01N/10	35.2N/100	71.23	+0.21
7‡	75.00	10	50	55.04N/10	49.4N/100	75.15	+0.15

‡ Note. In analyses Nos. 3 and 7, about 0.1 gram of crystallized copper sulphate was added, without, as may be seen, influencing the results. In another experiment, not recorded in the table, similar to No. 3 except that the copper was omitted, a solution of titanous chloride was substituted for the stannous chloride. In this case there was a negative error of 0.2 mg. in the arsenic. Twenty hours was required for the reaction, which is slower than when stannous chloride is used.

* One cubic centimeter of centinormal iodine solution = 0.15 mg. As.

† It is ordinarily easy to see when the reaction is complete. When the amount of arsenic is less than 5 mg., it is practically instantaneous.

solution by dissolving 9.900 grams of the oxide in sodium hydroxide solution, saturating with carbon dioxide and then making up to one liter. The amounts of arsenic which appear in column 1 of the table were obtained by measuring the appropriate volume of one of these solutions.

All volumetric apparatus employed was, of course, carefully standardized. The volumes of the standard solutions, as given in columns 4 and 5, are corrected for temperature and titre.

A somewhat similar process to that described in the present paper has been published by Engel and Bernard.* These authors reduced the arsenic with a mixture of hypophosphorous and hydrochloric acids and titrated the precipitated metal in essentially the same manner as that adopted by us. Their test analyses are very good on larger amounts of arsenic. They publish none for quantities less than 54 milligrams.

The reaction is very much slower than it is with stannous chloride. This necessitates allowing the mixture to stand for twelve hours and then boiling, a proceeding which may well result in loss of arsenious chloride.

It is far less easy to obtain hypophosphorous acid free from traces of arsenic than it is stannous chloride. The most important advantage which the use of the tin salt presents is probably to be found in the broad range of its applicability. In almost all of the salts which one ordinarily desires to subject to an arsenic determination, no other operation is required. Even compounds of lead, bismuth or antimony need no preliminary separation. We have found that titanous chloride (TiCl_3) may be substituted for the tin salt, but without advantage so far as known. It is probable that the lower chlorides of chromium, molybdenum, or vanadium would answer the same purpose, but they hold out no promise of superiority.

It is extremely likely that for the determination of fainter arsenical mirrors, obtained by the Marsh method, the iodometric titration will be found useful. A mirror of 0.01 mg. can scarcely be weighed satisfactorily, even with the best balance, because the weight of the tube when subjected to the action of the necessary reagents might change by an amount considerably in excess of the weight of the mirror. But it could be dissolved in millinormal iodine or starch iodide† and the excess titrated back by arsenite or thiosulphate of the same normality. For smaller mirrors than this, optical methods of comparison will still have to be used.

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* *Comptes rendus*, cxxii, 390, 1896.

† *Compare Zeitschr. f. anorg. Chem.*, xxvi, 180, 1901.