

XXXII.—*On the Electrolytic Test for Arsenic, and on the Presence of that Metal in certain Reagents.*

BY CHARLES L. BLOXAM.

IN a former communication upon this subject which I had the honour of presenting to the Society,† it was shown that when a solution containing arsenious acid is mixed with diluted sulphuric acid and subjected to the action of the voltaic current, arseniuretted hydrogen is evolved at the negative terminal, and that in this way very minute quantities of arsenious acid can be detected with great certainty, even in the presence of large quantities of organic matter, and without adding any material to the liquid which would interfere with its examination by other analytical processes. It was also stated that arsenic acid did not respond to this test, and that the presence of mercury in the liquid interfered very materially with the detection of the arsenic.

\* Handbuch. Bd. 3, s. 142.

† See page 12 of this volume.

It is the object of this paper to show how arsenic acid may be brought within reach of this test, how the interference of mercury may be prevented, and how all chance of error due to the evolution of antimoniuiretted hydrogen may be avoided.

The form of apparatus recommended in the previous notice admitted of some obvious improvements. A tube-funnel has been added, to permit the introduction of the liquid to be tested, and the platinum wires communicating with the battery have been replaced by broad strips of platinum foil.

If arsenious acid be converted into arsenic acid by boiling with hydrochloric acid and chlorate of potassa, and the solution be poured into the diluted sulphuric acid during the passage of the current, no arseniuretted hydrogen is evolved; but if a few drops of solution of sulphurous acid or of bisulphite of soda be poured down the funnel-tube, a greenish yellow iridescent crust of tersulphide of arsenic is almost immediately deposited at a little distance beyond the heated portion of the tube, and is followed, in most cases, by the usual mirror of metallic arsenic.

Since arsenic acid is reduced with great difficulty by sulphurous acid at the ordinary temperature, it appeared probable that the effect was really due to the hydrosulphuric acid formed by the action of the nascent hydrogen upon the sulphurous acid, and accordingly it was found that the introduction of a few drops of solution of hydrosulphuric acid into the electrolytic cell also caused the evolution of arseniuretted hydrogen.

If an excess of hydrosulphuric acid be employed, a deposit of sulphur is formed in the tube, nearer to the orifice than the deposit of sulphide of arsenic, from which it may be very easily distinguished by its much lighter colour, and by its insolubility in a warm solution of sesquicarbonate of ammonia, which readily dissolves the sulphide of arsenic.

Three experiments may be especially referred to in evidence of the certainty attending this process.

0.01 grn. of arsenious acid was boiled with hydrochloric acid and chlorate of potassa, and introduced into the electrolytic apparatus, and the reduction-tube through which the hydrogen escaped was heated to redness for 30 minutes without any appearance of deposit; but, on adding 5 grn. measures of a solution of bisulphite of soda, a yellow crust of tersulphide of arsenic made its appearance in 5 minutes, and was followed by a distinct deposit of

metallic arsenic, identified by its volatility and its solubility in chloride of lime.

In a second similar experiment, 10 grn. measures of a saturated solution of hydrosulphuric acid were poured down the funnel-tube, instead of the bisulphite of soda. The crust of sulphide appeared within 10 minutes, and that of metallic arsenic within 15 minutes.

A third experiment was made with only 0.001 grn. of arsenious acid which had been boiled with hydrochloric acid and chlorate of potassa; within 13 minutes after the addition of 10 grn. measures of hydrosulphuric acid, the yellow sulphide of arsenic appeared in the tube.

It was found that however large a proportion of hydrosulphuric acid was poured into the decomposing cell, the arsenic was still evolved, the metal combining with the nascent hydrogen in preference to the sulphur. It appeared probable, however, that the addition of hydrosulphuric acid would at once precipitate any antimony or mercury present in the liquid under examination, and would prevent their interference with the detection of the arsenic.

One grain of tartar-emetic (0.36 grn. Sb) dissolved in water, was slightly acidulated with sulphuric acid, mixed with an excess of hydrosulphuric acid, and poured, without filtering, into the decomposing cell in which the diluted sulphuric acid was undergoing electrolysis; the evolution-tube was maintained at a red heat for 38 minutes without any deposit in the tube except a thin film of white sulphur.

Another grain of tartar-emetic was then mixed with 0.01 grn. of arsenious acid, which had been boiled with hydrochloric acid and chlorate of potassa, and the mixture was treated with an excess of hydrosulphuric acid, and poured into the same decomposing cell without interrupting the experiment. In 5 minutes, yellow rings of tersulphide of arsenic made their appearance in the capillary reduction-tube; in less than 15 minutes, a distinct crust had formed, presenting exactly the same appearance as if no antimony whatever had been present. No deposit had been formed upon the negative plate.

In the next trial, only 0.001 grn. of arsenious acid was mixed with 1 grn. of tartar-emetic; the solution was boiled with hydrochloric acid and chlorate of potassa, diluted to one fluid ounce with

water, saturated with hydrosulphuric acid gas, and poured, with the suspended precipitate, into the decomposing cell. Within 15 minutes, a distinct deposit of metallic arsenic was obtained, which dissolved immediately in solution of chloride of lime.

When 1 grn. of tartar-emetic and 0.01 grn. of arsenious acid were mixed with considerable quantities of bread, milk, and beer, and the brown treacly liquid obtained by boiling with hydrochloric acid and chlorate of potassa, and subsequent evaporation, was mixed with excess of hydrosulphuric acid and poured into the decomposing cell, deposits of metallic arsenic and of the tersulphide were almost immediately formed in the tube. On collecting the dark precipitate after the operation, it was easily identified as sulphide of antimony.

In a second experiment of this description, one-fourth of the brown fluid (containing 0.09 grn. Sb and 0.0025 grn.  $\text{AsO}_3$ ) was introduced into the decomposing cell without adding hydrosulphuric acid, when a very distinct mirror of antimony was, of course, formed in the reduction-tube, and a deposit of that metal was obtained on the negative plate. The reduction-tube was then changed, and hydrosulphuric acid added, when deposits of arsenic and its sulphide, free from antimony, were formed in the tube.

To prove that with this modification of the test, the presence of mercury no longer prevented the detection of arsenic, experiments precisely similar to those above described were made, respectively, upon mixtures of 1 grn. corrosive sublimate with 0.01 grn. arsenious acid, and 0.25 grn. corrosive sublimate with 0.0025 grn. arsenious acid, mixed with white of egg, bread, milk, and beer, when no difficulty whatever was found in the detection of the arsenic.

The solution containing chloride of mercury and arsenic acid was electrolytised for half an hour without the slightest appearance of arsenical deposit in the heated tube, the mercury being deposited abundantly upon the negative plate; but on the addition of solution of hydrosulphuric acid, a crust of metallic arsenic was soon obtained.\*

\* It will be evident that this method of converting the arsenic into arsenic acid and precipitating the antimony and other metals by hydrosulphuric acid, in the *cold*, may be employed with advantage in Marsh's test; the solution containing the arsenic acid must be filtered, however, before introduction into the evolution bottle, as the suspended sulphide of antimony was found to be immediately decomposed in

In order to ascertain whether the occurrence of putrefaction in an organic mixture containing arsenious acid would interfere with its detection by the electrolytic test, an experiment was made with 0·001 grn. of arsenious acid mixed with meat, white of egg, beer, bread, and milk, and allowed to putrefy for nearly twelve months. No difficulty was experienced in detecting the arsenic.

I am very desirous of convincing myself that reliance may, in all cases, be placed on this process for the detection of arsenic, by operating upon organic matters *exactly similar* in their nature and quantity to those often submitted to the chemist in judicial inquiries, but have hitherto been unable to do this, in consequence of the difficulty of procuring hydrochloric acid so pure that, when examined in the large quantity required for the disintegration of considerable masses of viscera, it did not afford any indication of the presence of arsenic. Believing that I possessed a quantity of sulphuric acid perfectly free from arsenic, I employed it for the preparation of hydrochloric acid; but even this sample was not found to be absolutely free from the impurity, and on resorting to the sulphuric acid, the examination of a large quantity at once proved the presence of a very minute proportion of arsenic, which was more easily traced in the hydrochloric acid, since the latter could be employed without inconvenience in larger quantity, both in the electrolytic and in Marsh's test. The production of sulphuric acid absolutely free from arsenic is now engaging my attention.

It has also been incidentally noticed in the course of these experiments, that various samples of solution of potassa and of the solid hydrate contained very notable quantities of arsenic, attributable probably to their having been prepared from nitre by the action of (arsenical) copper at a high temperature.

A more important point for the consideration of the analytical chemist is the occurrence of arsenic in the hydrosulphuric acid,

contact with zinc and sulphuric acid. In a mixture containing a grain of tartar-  
emetic and one-hundredth of a grain of arsenious acid, the latter was detected as easily as if no antimony had been present, by boiling with hydrochloric acid and chlorate of potassa, precipitating the cold solution with excess of hydrosulphuric acid, filtering, and pouring into Marsh's apparatus.

In Marsh's test, the use of electrolytised zinc was found to be attended with advantage in minute investigation, on account of the very slow and steady evolution of gas.

prepared in the usual manner from sulphide of iron and diluted sulphuric acid. On passing the gas for 10 or 15 minutes through a reduction-tube heated to redness, a distinct crust of sulphide of arsenic was formed nearer to the heated portion than the deposit of sulphur. That the crust really consisted of sulphide of arsenic was proved by its solubility in carbonate of ammonia, and by its furnishing metallic arsenic when fused with carbonate of soda and cyanide of potassium in a current of carbonic acid. This experiment was repeated, with the same results, upon different samples of sulphide of iron and sulphuric acid. That the arsenic was due to the sulphide of iron, was ascertained by employing only so much of the purest sulphuric acid as gave no indication of arsenic in Marsh's process. Water saturated with the gas, when examined by Marsh's and the electrolytic test, was not found to contain arsenic.

No arsenic was detected in the washed hydrosulphuric acid gas prepared from native sulphide of antimony and hydrochloric acid.

---