CV.—The Electrolytic Estimation of Minute Quantities of Arsenic.

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THE estimation of minute quantities of arsenic has been improved in rapidity and reliability during the last few years by the practical application of electrolysis to the liberation of hydrogen and arsenic trihydride in place of the chemical method adopted in the Marsh-Berzelius test.

Already in 1861 an electrolytic method was described by Bloxam (Quart. Jour. Chem. Soc., 1861, 13, 12, and 338), but owing, largely no doubt, to the inconvenience of obtaining electrical energy from galvanic batteries—the only source practically available in those days—the method does not seem to have been generally adopted.

Since the epidemic of poisoning in Lancashire in 1900 due to accidental contamination of beer with arsenic, the testing of brewing materials for this poison has become a matter of considerable practical importance, and several chemists have carried out experiments with the electrolytic method.

Details of the application of this method in his laboratory were published by Trotman in July, 1902, in the *Brewers' Journal*, 1902, 445.

In consequence of the appointment of the Royal Commission on Arsenical Poisoning, the electrolytic process was carefully investigated in the Government Laboratory, and a method for the electrolytic estimation of minute quantities of arsenic, more especially in brewing materials, was described by Thorpe in August, 1903 (Trans., 1903, 83, 974).

These investigators employed platinum cathodes, with this difference,

however, that Trotman recommends the addition of zinc sulphate to the electrolyte under examination.

In Thorpe's communication, special attention is drawn to the fact that arsenates are not reduced in his apparatus. He therefore recommends that the substance under examination should be treated with nascent sulphurous acid before introduction into the electrolytic vessel. The same preliminary treatment was recommended by Bloxam, who also clearly recognised the difficulty of reducing arsenates electrolytically. Even the effect of mercury in hindering the detection of arsenic, which has been fully examined in the present investigation, was already pointed out by Bloxam, and a method for dealing with solutions containing arsenates in presence of antimony and mercury was elaborated by him.

In Trotman's communication no preliminary treatment of the material examined is recommended, and no mention is made of the difficulties due to the presence of arsenates. As will be seen from the present paper, however, a platinum electrode in the presence of zinc sulphate as recommended by Trotman behaves as a zinc electrode and is capable of reducing arsenates. In fact, the authors are in a position to state that both platinum and zinc electrodes were experimented on by Trotman, the former being unsatisfactory whilst the latter gave satisfactory results. Owing to the obvious inconvenience of employing a soluble electrode composed of a material not easily obtained free from arsenic, the zinc electrode was, on the recommendation of one of the authors of the present paper, replaced by one of platinum electrolytically coated with zinc by the addition of zinc sulphate to the electrolyte under examination.

Since the completion of the following investigation the use of zinc electrodes for arsenic testing has been recommended by Mr. W. Thomson, who also finds that arsenates are reduced by them (*Mem. Manchester Phil. Soc.*, May, 1904, 17, 48.)

In the present investigation, the manner in which the nature of the electrode and other conditions affect the production of hydrogen arsenide by electrolysis of arsenates and arsenites has been fully examined, and as a result suggestions have been made for the further simplification of the electrolytic estimation of minute quantities of arsenic, and certain possible sources of error in the method are indicated.

The influence of the material of the cathode may be classified under the two headings of "supertension" and catalysis. The supertension ("Ueberspannung." Caspari, Zeit. physikal. Chem., 1899, 30, 89) of an electrode is the excess of electromotive force necessary for the liberation of hydrogen at that electrode over the electromotive force required for the reversible production of hydrogen on a cathode of

platinised platinum. As is well known, this excess is due to the resistance offered to the production of gas bubbles in the liquid, and varies with the nature of the electrode in contact with it. Hydrogen evolved with a high supertension, possessing a large amount of free energy, has the thermodynamic properties of enormously compressed gas, and before its liberation in bubbles the layer of liquid immediately adjoining the electrode as well as the metal of the electrode itself no doubt becomes enormously supersaturated with the gas. As a result, such hydrogen is capable of effecting reductions requiring a large amount of free energy, and it has, for example, been shown by Tafel (Zeit. physikal. Chem., 1900, 34, 227) that the reduction of caffeine depends to a very large extent on the supertension of the electrode employed. The supertension (in volts) of the most important metals having been determined by Caspari (loc. cit.) in Nernst's laboratory in the following order : platinised platinum, 0.005; smooth platinum, 0.09; nickel, 0.21; copper, 0.23; tin, 0.53; lead, 0.64; zinc, 0.70; mercury, 0.78, it is possible to predict, with a fair amount of certainty, the behaviour of an electrode during reduction with regard to this effect.

The thermodynamic efficiency of electrolytic hydrogen, which is limited by the magnitude of the supertension of the electrode, is, however, not the only influence determining electrolytic reduction. Catalytic effects due to the metal of the electrode, and often also to substances in solution, play an important part as well, and these catalytic effects may vary in different cases, and can, therefore, not be predicted like those due to supertension.

In the present case, we have been able to show that the reduction of very small quantities of arsenate to arsenite probably requires a large supertension, for this was only accomplished by the metals having a large supertension, such as lead, zinc, and also by iron in the form of wire.* Platinum, on the other hand, which has a low supertension, proved inefficient even for very considerable concentrations of The production of hydrogen arsenide from arsenites, arsenates. however, depends on other influences besides supertension, for this could be accomplished with smaller concentrations of arsenious acid when platinum electrodes were employed than when those of copper with a much larger supertension were used. Moreover, mercury electrodes, having the highest supertension of all the metals, proved to be utterly inefficient. As will be seen in the sequel, it was possible to reduce arsenates or arsenites by their means to metallic arsenic, but impossible to convert the latter into arsenic trihydride. Even the production of arsenic trihydride from arsenites, however, seems

* The supertension of iron in acid solution has not been recorded by Caspari, but its efficiency as an electrode agrees with Tafel's observation.

to require a certain amount of supertension, for when electrodes of platinum coated with platinum black were employed, none of the trihydride was produced. This circumstance corresponds with Thorpe's observation that platinum electrodes become inefficient when they are roughened by prolonged use.

The apparatus employed for the experiments was, with the exception of the electrodes, identical with the form recommended originally by Trotman. A diagram illustrating the modification recommended by us with lead electrodes is given at the end of the present paper. The cathode chamber consisted of a glass cylinder, 3 to 4 cm. in diameter and 16 cm. in height, closed at one end by a porcus partition of parchment paper,* at the other by an india-rubber bung, through which passed the electric connection to the electrode, a tap funnel for the introduction of the liquid to be examined, and a thermometer. The evolved gases passed through a side-tube into a drying tube containing a cotton wool plug, calcium chloride, and lead acetate paper, and then through the Marsh-tube.

Where not specially stated to the contrary, the anode consisted of a platinum band; the cathode of the metal examined had as nearly as possible the same effective surface in all experiments, being either a rod, hollow cylinder, or spiral of about 2 cm. in diameter and 3 cm. in The strength of the current which was taken from the lightheight. ing mains through a lamp resistance was 5-6 amperes. The electrolyte in all the experiments on acid solutions was a 10 per cent. solution of sulphuric acid. A blank experiment lasting twenty to thirty minutes was always performed before the standard solution containing the arsenic was introduced. The latter was made up in various strengths with sodium hydrogen arsenate for the experiments on arsenates and with arsenious oxide for those on arsenites. Experiments were at first carried out under the ordinary working conditions with the apparatus surrounded by ordinary cold water. In this case, the temperature in the cathode compartment varied from 15-50°. Experiments were then made at $0-5^{\circ}$, pieces of ice being placed in the anode and cathode compartments; and, lastly, the temperature of the cathode compartment was raised to about 97°, the liquid in the anode compartment being heated to boiling. All the recorded determinations Preliminary experiments showed that were repeated at least once. with a non-sensitive electrode, the whole of the arsenic is not removed from the solution as arsenic trihydride, the mirror obtained corresponding in intensity with only a part of the arsenic. Thus, when a spiral of copper wire was employed as a cathode and 0.00001 gram of arsenious oxide was added, a mirror corresponding with only half that

• For the advantages of a parchment-paper partition, see Trotman, J. Soc. Chem. Ind., 1904, 23, 178.

quantity was obtained. On changing the Marsh-tube after this and continuing the passage of the current, no more arsenic was deposited; when, however, small quantities of the oxide were added, these additions were detected in full. It may therefore be concluded that each electrode will only detect quantities of arsenic above a certain lower limit peculiar to itself, and that it is possible to compare the efficiency of electrodes by comparing the sizes of mirrors obtained after the introduction of the same initial amount of arsenic. The standard mirrors for these experiments were prepared in an electro-



lytic apparatus with platinum electrodes, the arsenic being added in the arsenious state.

The Tables I, II, and III show the results obtained, quantities being stated in terms of 0.000001 gram of arsenious oxide. The details regarding the electrodes are as follows:

Tables I and III, electrodes of single metal.

Platinum : hollow cylinder, height 4 cm., diameter 2 cm.

Platinised platinum: same electrode coated with platinum black, according to Lummer and Kurlbaum (Kohlrausch und Holborn, Leitvermögender Elektrolyte, p. 9). Copper: spiral of $1\frac{1}{2}$ mm. wire, height and diameter the same as the platinum cylinder.

Iron: spiral of pure thin wire wound round glass rods, height and diameter approximately the same as above.

Zinc: solid cylinder of the shape illustrated in Fig. 2, diameter and height as above.

Lead: same shape as zinc. (1) With ordinary smooth surface, (2) roughened by alternate electrolytic oxidation and reduction.

Mercury: contained in small flat crystallising dish of about 3 cm. diameter, the current being introduced by means of platinum wire fused into a glass tube.

Table III. Platinum electrode as above, 10 c.c. of 10 per cent. solutions, or, where this was not possible, of saturated solutions of the salts stated in the table, having been added to the electrolyte.

The main features of the results revealed by the tables have already been summarised, but certain points called for further investigation. The most important of these was the lack of efficiency of the mercury electrode in spite of its high supertension. A quantity of 0.0001 gram of arsenic was therefore introduced into the apparatus in the state of arsenate, the cathode being mercury. After the current

TABLE I.

Experiments with minute quantities of arsenic. Solid cathodes. Quantities stated in terms of 0.000001 gram of As_2O_3 .

Electrode.	Arsenite added.	Arsenite de- tected.	Temperature.	Duration of ex- periment in minutes.	Arsenate added.	Arsenate de- tected.	Temperature.	Duration of ex- periment in minutes.
Platinum (smooth)	5 5	5 2	0—5° 97	35 30	5 5	0 0	0—5° 97	30 30
Copper	6 6	1 1	$0-5 \\ 97$	30 30	6 6	1 1	0 <u>-5</u> 97	30 30
Iron	5 5	5 5	$0-5 \\ 97$	30 30	5 5	5 5	0 <u>-5</u> 97	30 30
Lead (smooth)	5 5	5 5	05 97	30 45	5 5	5 5	0 <u>-5</u> 97	30 45
Lead (roughened)	5	5	0—5	30	5	5	0-5	30
Zinc	5 5	5 5	0 <u></u> 5 97	30 30	5 5	5 5	0 <u>-5</u> 97	20 20
Mercury	5 5	0 0	0 <u>-5</u> 97	30 30	5 5	0	0 <u>-5</u> 97	30 30

TABLE II.

Experiments with platinum cathode coated electrolytically with other metal by the addition of a salt solution. Quantities of arsenic in terms of 0.000001 gram of As_2O_3 .

Salt addad	Arsenite		Tempera-	Arse	Tempera-		
Salt added.	Added.	Detected.	ture.	Added.	Detected.	ture.	
$\begin{array}{c} \mathrm{CuSO}_4 & \dots \\ \mathrm{feSO}_4 & \dots \\ \mathrm{PbAc}_2 & \dots \\ \mathrm{ZuSO}_4 & \dots \\ \mathrm{HgCl}_2 & \dots \\ \mathrm{HgCl}_2 & \dots \\ \mathrm{NiSO}_4 & \dots \\ \end{array}$	6 5 5 5 5	1 5 5 5 0	0—5° ,, ,, ,,	5 1 1 1 1 1 1	0 0 1 1 0 0	15—50° ,, ,, ,, ,,	

TABLE III.

Experiments with inefficient electrodes and larger quantities of arsenic, approximate limits below which arsenic was not detected. Quantities stated in terms of 0.000001 gram of As_2O_3 .

Electrode.	Arsenite, limit.	Arsenate, limit.	Temperature.		
Platinum (smooth)		200 200	05° 97		
Platinum (platinised)	above 500	above 500	0—5° 97		
Mercury	3000—5000 ,, ,,	3000—5000 ,, ,,	0—5° 97		

had passed for five minutes the mercury was removed, carefully washed with water, and then shaken thoroughly with some bleaching powder solution, one-third of the latter being then tested for arsenic in the usual manner, when the mirror obtained was too intense for accurate estimation. Careful blank experiments had been made with the mercury and other chemicals to prove their original freedom from arsenic. This experiment proves that the difficulty in the use of a mercury electrode is not to be found in its incapacity to reduce arsenates to metallic arsenic, but in the difficulty of converting the latter into arsenic trihydride. No doubt this is largely due to the fact that the arsenic dissolves in the mercury, and thus to a great extent escapes the action of the nascent hydrogen.

The conclusion drawn was further confirmed by an experiment in which 0.00004 gram of arsenic was added, and the current passed for 1 hour. No mirror was obtained, but nevertheless all the arsenic must have been reduced to the metallic state, and thus removed from the liquid, for when the latter was tested it was found to be quite free from arsenic.

The cause of the inefficiency of copper as an electrode for quantities of arsenate and arsenite below about 0.000005 gram of arsenious oxide was also investigated more closely. For this purpose a quantity of 0.00001 gram of the oxide was introduced into the apparatus and electrolysed for two hours with a copper cathode. A mirror corresponding in intensity with only about half the substance added was obtained. All the arsenic had nevertheless been removed from the liquid, for when the latter was examined by means of the lead apparatus recommended at the end of the paper it was found to contain no arsenic. The same experiment was then carried out with the single difference that sodium arsenate was substituted for the arsenious oxide. In this case, however, all the arsenic was not removed from the solution, for when the latter was tested in the lead apparatus it gave a mirror corresponding with about 0.000002 gram of arsenic. It may, therefore, be concluded that a copper cathode will completely reduce arsenious acid, but that part of the arsenic reduced remains as metallic arsenic, and is not converted into arsenic trihydride. On the other hand, probably owing to lack of sufficient supertension, arsenates are not completely reduced by means of a copper electrode.

The experiments recorded in Table I show that the electrodes most sensitive for very minute quantities of arsenic in the state of arsenate are those of lead, zinc, and iron (as wire). The last two being soluble in the electrolyte are manifestly inconvenient for practical use. Lead, on the other hand, being insoluble both as an anode and as a cathode is an exceedingly suitable metal. Its cheapness is an additional advantage, and when carefully selected it is possible to obtain commercial samples absolutely free from arsenic and antimony. The experiments of Table II demonstrate the correctness of the principle underlying Trotman's method that platinum electrodes may be employed for the detection of minute quantities of arsenic in the state of arsenate when zinc salts are added. Lead salts may also be employed but are less convenient, owing to the precipitate of lead sulphate which is formed when they are introduced into the electrolyte. Iron salts do not affect the platinum electrodes either for the detection of

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arsenates or arsenites. This may perhaps be due to the difficulty of obtaining a deposit of iron on the platinum.

In order further to test the suitability of lead as an electrode for the detection of arsenic, various substances, such as mineral and vegetable oils and metallic salts were added to the electrolyte. The

TABLE IV.

Experiments with a lead cathode and anode with various added Ordinary working temperature 15-50°. Quantities in substances. terms of 0.000001 gram of As₂O₃.

	Arse	enite	Arsenate		
Substance added.	Added.	Detected.	Added.	Detected.	
Vaseline in ether	1 1 1 5 1 1 1 1	1 1 1 0 0 0 0 0 0 0	1 1 1 5 5 10	1 1 1 0 0 0 0 0 0	
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\frac{5}{5}$	5 5 0	1 1 1 5	1 1 1 0	

oils were without effect, but as was to be foreseen the metallic salts, excepting those of lead and zinc, render the electrode inefficient. Their influence can, however, be neutralised by the simultaneous addition of a solution of lead acetate (or zinc sulphate) in all cases except where Extreme caution is therefore necessary if mercury salts were present. mercury is employed for making electric connections, for special experiments showed that so small a quantity as one centigram of mercuric chloride is sufficient to destroy utterly the sensitiveness of an electrode. Table IV. shows the results of experiments.

A final series of experiments was carried out with electrodes of lead, zinc, and platinum in alkaline solutions (25 per cent. solutions of caustic soda). The lead and zinc cathodes were not sensitive under these conditions, and those of platinum were utterly useless. The lower limit, which could be detected at 0° and 100° with solutions of arsenites and arsenates was about 0.000015 gram for lead and zinc, and about 0.002 for platinum.

As a result of the foregoing investigation, we are able to recommend the use of lead electrodes for the detection of minute quantities of arsenic by electrolysis. The appended figures will explain the apparatus in the form in which it is in use in Mr. Trotman's laboratory in Nottingham at the present time. With slight modifications it has been employed for about four months with unvarying success; about 1800 determinations having been made. During a fortnight all results were checked, firstly, by electrolysis in an apparatus with platinum electrodes, the substance examined having been previously reduced with potassium metabisulphite and sulphuric acid according to Thorpe's process, and, secondly, they were checked according to Trotman's method in an apparatus with a platinum cathode, zinc sulphate (in some cases also lead acetate) being added. Upwards of 140 determinations were checked in this manner, the results obtained by the three methods being in every case identical. The apparatus is extremely sensitive, it being possible to detect with certainty 0.0000005 gram of arsenic in 50 c.c. of liquid. As examples of the use of the apparatus we give the methods employed for the estimation of arsenic in malt and beer.

Malt: forty grams are thoroughly shaken in a beaker with 100 c.c. of a 10 per cent. solution of sulphuric acid and heated on the water-bath for 20 minutes with occasional shaking, the beaker being covered, and the temperature not being allowed to rise above $50-60^{\circ}$ in order to minimise evaporation. Fifty c.c. of the solution are then introduced into the apparatus, a few drops of amyl alcohol being added to prevent frothing. Half an hour is allowed for the total deposition of the arsenic.

Beer: ten c.c. of strong H_2SO_4 are added to 50 c.c. of the beer, and introduced into the apparatus, together with a few drops of amyl alcohol, half an hour being allowed for the deposition of the arsenic.

Details of Apparatus.

FIG. 4. A. Cooling vessel for water, conveniently replaced by an insulated lead trough, when several sets of this apparatus are being used simultaneously.

B. Anode compartment.

C. Anode of lead (view in Fig. 1), lid-shaped, to minimise spraying of acid, with a slot to allow cathode to be observed, height 5", inner diameter 2", bent inwards at the bottom to support the cathode compartment, the latter being conveniently placed on a glass-rod triangle (not shown in figure) to allow bubbles of oxygen to escape more readily.

D. Cathode compartment, glass cylinder, width $1\frac{1}{2}$ ", height 7", closed at one end by an india-rubber stopper, at the other end by arsenic-free parchment paper, tied

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while wet by means of string and kept in its place by the flange on the end of the cylinder.

E. Cathode of pure lead, solid. Height 1", thickness $\frac{2}{4}$ ". Length of stem 7". View in Fig. 2.*

F. Funnel, with wide stem, having graduations of 10 c.c., 25 c.c., 50 c.c., closed by a ground-glass rod.

G. Drying tube charged with (a) lead acetate paper, (b) calcium chloride, and (c) plug of cotton wool.

H. Shield to protect bunsen burner from draughts. View in Fig. 3.



FIG. 4.

Current: about 5-6 amps., that is, for single apparatus 9-10, thirty-two candlepower lamps on a 200 volt circuit.

Electrolyte : anode solution : 10 per cent. sulphuric acid. Cathode solution : liquid under examination. Temperature, 15-50°.

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* As new cathodes often contain arsenic on the surface; they should be thoroughly scraped and cleaned by immersion in boiling strong nitric acid for three or four minutes and subsequent washing with water. They should be perfectly bright, and give a negative result after a blank experiment lasting one hour.