## 974 THORPE: THE ELECTROLYTIC ESTIMATION OF

## XCIV.—The Electrolytic Estimation of Minute Quantities of Arsenic, more especially in Brewing Materials.

By T. E. THORPE, C.B., F.R.S.

THE Royal Commission on Arsenical Poisoning, in their First Report, recommended that the Board of Inland Revenue should possess and should exercise powers to specify the ingredients of beer, and the materials used in their preparation which are liable to be contaminated by arsenic, and to prescribe tests by which their freedom from arsenic may be ascertained.

With a view to the carrying into effect of the above recommendation, the Board of Inland Revenue, with the approval of the Treasury, decided to appoint a Committee to advise them as to the tests which might properly be prescribed for the several ingredients of beer which may be held to be liable to contamination.\*

In their Report to the Board, the Committee state that of the various methods which have been suggested from time to time for the detection and estimation of the relatively small quantities of arsenic which may be present in beer and the ingredients of beer, or in the materials which may be used in their preparation, they are of opinion that those methods which depend on the conversion of the arsenic into hydrogen

\* The Committee consisted of :

T. E. Thorpe, Esq., C.B., F.R.S., Principal of the Government Laboratory, as Chairman.

Professor William Augustus Tilden, D.Sc., F.R.S.

Professor Harold Baily Dixon, M.A., F.R.S.

Graham Aldous, Esq.

John Pattinson, Esq., F.I.C., with

Mr. T. J. Cheater, of the Government Laboratory, as Secretary.

arsenide and the subsequent deposition of the arsenic in the elementary form by heating the gas are, on the whole, to be preferred.

The hydrogen arsenide may be formed in practice by the action of so-called "nascent" hydrogen on the arsenic present. The hydrogen may be evolved either electrolytically or through the agency of dilute hydrochloric acid on zinc admixed with, or containing, such an amount of copper or other suitable metal as to give rise to a sufficiently rapid evolution of the gas.\*

The amount of arsenic deposited by heating the hydrogen arsenide so formed is then determined by comparison with deposits obtained in precisely the same manner from wort, beer, malt extracts, sugar solutions, &c., containing known quantities of arsenic.

An electrolytic method for detecting arsenic appears to have been first suggested by the late Professor Bloxam, of King's College (Quart. Journ. Chem. Soc., 1861, 13, 12 and 338), but in its original form it had several disadvantages which have prevented it from being generally adopted by chemists. Modifications of it have been made by Mr. Trotman, Mr. Bevan, and others. The process has been carefully investigated in the Government Laboratory, and in the form now described it is easy of application, and is capable of giving trustworthy results with a comparatively small expenditure of time and trouble.

The apparatus employed in the electrolytic method consists of the following parts :

1. A. glass vessel, A, provided with a ground-glass stopper and connections, B, and a drying tube, C, containing calcium chloride.

- 2. A porous cell, D.
- 5. A hard glass constricted tube, G.
- 3. A glass vessel, E.
- 6. A small Bunsen burner, H.

4. A cooling\_vessel, F.

The glass vessel, A, forms with the porous vessel, D, the inner cell for the cathode where the hydrogen and hydrogen arsenide are produced on passing the electric current. The vessel, A, is open at the bottom and fitted at the top with the ground-glass stopper, B, through which is passed, to a point just below the neck of the vessel, the stem of the tap-funnel. The glass stopper also carries the gas exit tube on which is a bulb. The tube is bent as shown in the drawing, and is connected by means of a ground-glass joint with the drying tube, C. Through the glass cap is fused a stout platinum wire for making the connection on the outside with the current, and within the vessel with the electrode.

The inner electrode, forming the cathode, is of sheet platinum and cone-shaped, with several perforations. It is suspended from a hook made on the end of the wire passing through the glass stopper, and is

\* In the case of the electrolytic method, it is necessary that the arsenic should be in the condition of an arsenite or arsenious acid.

adjusted so that when the stopper is inserted in the vessel the lower edge of the electrode is 1 mm. above the bottom of the vessel, A. It is then securely attached to the wire by closing the hook.\*

The porous vessel, D, is larger by 2 to 3 mm. in diameter and in depth than the cylindrical portion of the glass vessel, A. As seen in the figure, A rests by means of its bulged-out shoulder upon the upper edge of D. The porous vessel is of unglazed, highly silicious ware, of the composition employed for the well-known biscuit filters, first made by Dr. Pukal, and is from 1 to 1.5 mm. in thickness.<sup>+</sup>

The cell for the anode consists of the stout glass vessel, E, upon the flat bottom of which the porous vessel, D, containing the glass vessel,



A, stands. The anode consists of a band of platinum, 2 cm. broad, passing loosely round the porous cell, and connected with the current by means of a stout platinum wire. The liquid in the vessel, E, should

· Care must be taken that the hook is effectually closed and the contact complete, otherwise there may be danger of sparking, which might bring about an explosion if the apparatus contained a sufficient proportion of air.

By continued use, the surface of the cathode loses its polish, and the metal becomes coated with a grey powder, especially on the inside of the cone. In these circumstances, the deposit which forms, especially from some saccharine liquids. may retain arsenic. Care should be taken, therefore, that the cathode is re-polished from time to time. After this operation, it is advisable to immerse the cathode completely in the dilute acid and subject it to the action of the current for, say, half an hour.

+ The porous vessel may gradually become more or less stained, especially when used with caramels, black beers, and other highly coloured liquids. It is advisable, therefore, from time to time, to heat the vessel in a muffle furnace.

be kept below  $50^{\circ}$ , and the vessel is therefore placed in a larger dish, F, containing cold water.

The drying tube, C, is packed as follows: A plug of cotton wool is first inserted, and then pure granulated, anhydrous calcium chloride,\* in pieces about the size of small shot or malt grains; for a length of 5 cm. Another loose plug of cotton wool is placed upon the calcium chloride, followed by a roll of lead acetate paper. This is prepared by soaking filter paper in a cold saturated solution of lead acetate and then drying the paper in air. The paper is cut into strips about 1 cm. broad and rolled into a coil fitting loosely in the tube. A small, spiral coil of lead acetate paper is also placed within the enlarged end of the exit tube to which the calcium chloride tube is attached.

To the end of the drying tube, there, is fixed by means of a short piece of unvulcanised rubber tubing, the hard glass constricted tube in which the arsenic is to be deposited. The ends of the drying tube and the hard glass tube should be in close contact beneath the rubber. To make one of these tubes, a piece of Jena glass tubing having an external diameter of 5 mm. and an internal diameter of 3.5 mm. is cleaned by successive treatment with acid, water, and alcohol, and dried. It is then held in the blow-pipe flame, so that a portion of the tube about 2 cm. in length and 5 cm. from the end of the tube is thoroughly softened, when the heated portion is drawn out to a length of 7 to 8 cm., and having at a distance of 1 cm. from the shoulder of the tube an external diameter of 2 mm., a size which should be maintained as nearly as possible throughout the length of the constricted The tube is cut off near the end of the drawn-out portion, the part. last 1 cm. of which is turned up at right angles. The hard glass tube is supported in a horizontal position, when attached to the drying tube of the apparatus, by resting in the slots on the upper edge of the cone which surrounds the flame of the small Bunsen burner. A piece of platinum gauze about 2 cm. square is wrapped round the hard glass tube at the point where it is to be heated by the Bunsen flame.

The small Bunsen burner has a circular base 12 mm. high, and its tube is 6 cm. in height and 5 mm. in internal diameter. The upper portion of the tube is threaded and carries a gallery upon which rests a copper cone. The upper edge of the cone contains two slots to receive the hard glass tube.

The apparatus, when employed in the manner to be described, has an apparent resistance of 1.4 ohms, the potential difference between the ends of the wires of the poles being 7 volts with a current of 5 amperes. This strength of current gives about 40 c.c. of hydrogen in

<sup>\*</sup> Where a series of experiments is carried out with the same apparatus, the calcium chloride should be renewed from time to time, say, after three or four experiments.

a minute, which furnishes a steady flame about 2 mm. in height, and is the strength of current recommended to be used for the purposes of the test. To effect the reduction of the intensity of the main laboratory supply, which is the most convenient source of the current, a rheostat of incandescent lamps may be employed. The lamps are arranged in parallel with each other, but in series with the apparatus, and, according to the current desired, lamps of different candle power may be inserted. An ammeter is included in the circuit.

The apparatus may be arranged for the simultaneous execution of a number of tests. By suitable construction on the charging board, the electric current passes through the solutions arranged in series, and any of these may be brought into or cut out of the circuit as desired. The current is brought to the required strength—4.5 to 5 amperes by the introduction in the rheostat of lamps of the requisite power according to the number of tests to be carried out simultaneously. A diagram illustrating the method employed for this purpose is shown in Fig. 2 (p. 979).

The sulphuric acid solution employed in the apparatus is prepared by mixing one volume of pure concentrated sulphuric acid with seven volumes of water. It must, of course, be tested to ascertain its freedom from arsenic before it is used.\*

Certain of the solutions to be tested are very liable to froth when introduced into the apparatus. This inconvenience may be obviated by adding one or two c.c. of rectified amyl alcohol (b. p. 128—132°) to the acidified liquid undergoing electrolysis.

Before describing the application of the test, it will be convenient to give in detail the methods to be followed in preparing the extracts or solutions of the various substances in such a form and in such an amount as to render them suitable for testing.

(1) MALT.—Unground malt may readily be examined for arsenic by washing the malt with warm dilute acid and testing the acid extract, but this method is inconvenient in the case of a ground or crushed malt, as it is difficult to obtain a suitable extract. A ground malt is therefore incinerated in presence of lime and magnesia and the solution of the ash tested. Direct experiment has shown that deposits of arsenic obtained after treatment of an unground malt with dilute acid are equal in intensity to those obtained by the basic method of treatment of the same malt. The two methods are as follows :

<sup>\*</sup> It is advisable to saturate the stock quantity of the dilute acid with the products of its electrolytic decomposition before use in the apparatus. This may be conveniently effected from electrodes of platinum wire immersed in the liquid. The advantage of this procedure is, that it destroys any trace of dissolved sulphurous acid, and thereby obviates the formation of sulphuretted hydrogen during the actual testing.

Basic Method for Ground Malt.—Ten grams of the ground malt are transferred to a porcelain, or preferably a platinum, dish about 3



Diagram of the rheostat and charging board arranged for four simultaneous tests. The arrows show the direction of the current.

a, a, a, a.-Lamps by means of which the current is reduced to the required strength.

b, b, b, b.-Switches.

c.---Ammeter.

d, d, d, d.-Electrolytic cells as in Fig. 1.

inches in diameter, 30 c.c. of arsenic-free lime water\* are added, and the dish heated over a small Bunsen flame for a few minutes. About

• The lime-water, lime, magnesia, and potassium metabisulphite are tested as to their freedom from arsenic by the method described under "Chemicals" (pp. 981, 982).

0.5 gram of arsenic-free magnesia or lime is then added and thoroughly mixed with the contents of the dish, the heating of which is continued until the organic matter is completely charred. The dish is then placed in a muffle furnace, or over a low Bunsen flame and heated at a dull red heat until practically all the carbon is burnt off. When cold, the ash is moistened with water and 20 c.c. of the dilute sulphuric acid added. The dish is warmed and the contents trans-About half a gram of potassium metaferred to a 4 oz. flask. bisulphite is added, and the solution boiled until free from sulphurous acid. After cooling, the solution is ready to be tested.

Acid Method for Unground Malt .-- Forty grams of malt are transferred to a wide-mouthed, stoppered bottle. Forty c.c. of the dilute sulphuric acid and 60 c.c. of water are mixed together, raised to a temperature of 50°, and added to the malt. The bottle is shaken at intervals during 20 minutes and the liquid poured off; 25 c.c., representing 10 grams of malt, are transferred to a small flask, half a gram of potassium metabisulphite added, and the solution boiled until free from sulphurous acid. When cold, the solution is used for the test.

(2) MALT SUBSTITUTES (Glucose, Invert Sugar, Caramel, &c.).-Five grams are weighed in a small flask and dissolved in 20 c.c. of water. Half a gram of potassium metabisulphite and 5 c.c. of the dilute sulphuric acid are then added and the solution boiled until free When cold, it is ready for adding to the from sulphurous acid. electrolytic apparatus.

(3) WORT.-Direct experiments have shown that when using the electrolytic apparatus it is unnecessary to destroy the organic matter of the wort. All the arsenic which may be present is evolved as hydrogen arsenide.

For the test, 25 c.c. of the wort are placed in a small flask, half a gram of potassium metabisulphite and 5 c.c. of the dilute sulphuric acid are added, and the solution boiled until free from sulphurous acid. When cold, the solution is used for the test.

(4) HOPS AND HOP SUBSTITUTES .- Five grams of the substance, ground if necessary in a mortar, are placed in a platinum dish, treated with lime and magnesia and incinerated, and the examination for arsenic carried out in the same manner as described in connection with ground malt.

(5) BEER. - Direct experiments have shown that when the electrolytic apparatus is used it is unnecessary to destroy the organic matter All the arsenic which may be present is evolved as of the beer. hydrogen arsenide.

Twenty-five c.c. of beer are placed in a small flask, half a gram of

potassium metabisulphite and 5 c.c. of dilute sulphuric acid added, and the solution boiled until free from sulphurous acid. The cold solution is used for the test.

(6) YEAST AND YEAST FOODS.—Five grams are introduced into a flask and gently warmed with 20 c.c. of water. Half a gram of potassium metabisulphite and 5 c.c. of dilute sulphuric acid are then added, and the contents of the flask boiled until free from sulphurous acid. The cold solution is used for the test.

Of liquid yeast foods, 25 c.c. are taken and the solution boiled, after the addition of potassium metabisulphite and sulphuric acid, until free from sulphurous acid.

(7) CHEMICALS:

(a) Sulphites.—Of solid sulphites, 1 gram is dissolved in 25 c.c. of water in a small flask. Five c.c. of dilute sulphuric acid are added and the solution boiled until free from sulphurous acid. The cold solution is used for the test.

Of solutions of sulphites, 25 c.c. are taken and boiled in like manner after the addition of 5 c.c. of dilute sulphuric acid. The liquid is tested by the addition of a little more sulphuric acid to ascertain if the whole of the sulphite has been decomposed.

(b) Acids.—Sulphuric Acid.—Five c.c. are diluted with 20 c.c. of water, half a gram of potassium metabisulphite added, and the solution boiled to expel sulphurous acid. When cold, the solution is used for the test.

Hydrochloric Acid.—Five c.c. are placed in a porcelain dish and diluted with about 5 c.c. of water. Five c.c. of pure nitric acid (sp. gr. 1.4) and 2 c.c. of pure concentrated sulphuric acid are then added, the dish placed on a sand-bath, and the liquid evaporated until the sulphuric acid fumes. The dish is removed, and, when cold, about 20 c.c. of water and half a gram of potassium metabisulphite added. The solution is transferred to a flask and heated until free from sulphurous acid and then tested.

(c) Sulphur.—Ten grams are taken, and the examination for arsenic carried out by burning the sulphur in a current of oxygen in the manner described in connection with the estimation of arsenic in fuel (this vol., p. 969). Owing to the readiness with which sulphur sublimes, the temperature to which the hard glass tube is heated should be as low as possible consistent with the burning of the sulphur, and the empty portion of the hard glass tube, next to the bent and drawn-out end, should not be heated until the sulphur in the other part of the tube has been burnt. The liquid in the absorption tube is boiled to expel sulphurous acid, and any sulphur or other solid substance which may have passed into the absorption tube in the process of combustion is rendered soluble and in suitable condition for addition to the electrolytic apparatus by the method described for treating the ash of fuel.

(d) Other Chemicals.-Of solids, 1 gram is taken and dissolved in 25 c.c. of water. Of liquids, 25 c.c. are taken. In either case, if the solution is alkaline, it must be neutralised by the addition of dilute sulphuric acid. To the neutral liquid, half a gram of potassium metabisulphite and 5 c.c. of dilute sulphuric acid are added, and the solution boiled until free from sulphurous acid. The cold solution is used for the test.

8. FININGS .- Five grams are weighed out in a flask, 20 c.c. of water added, and gently warmed to effect solution. If sulphurous acid or a sulphite is present, 5 c.c. of the dilute sulphuric acid are added, and the solution boiled until free from sulphurous acid.

If no sulphurous acid is present in the finings, half a gram of potassium metabisulphite is added to the solution prepared as above, together with 5 c.c. of the dilute sulphuric acid, and the solution boiled to expel sulphurous acid and then tested.

## Mode of Working.

The electrolytic apparatus, as already described, is arranged for the test, which is carried out in the following manner. The cells, electrodes, and glass vessel, A, with the cap, funnel, and exit tube, are thoroughly cleaned and rinsed with distilled water. The porous vessel, D, containing the vessel, A, is placed in E, which is surrounded by cold water contained in the glass dish, F. The calcium chloride tube, C, which has been packed in the manner described, is fitted on the ground glass connection. The hard glass tube, G, is attached by the indiarubber connection to the drying tube so that the bent portion at the end is in an upright position, and the platinum gauze is so arranged on the tube that it just overhangs the shoulder. The small Bunsen burner, H, is placed beneath the tube, which rests in the slots on the upper edge of the cone in such a position that when lighted the flame will heat about 2 cm. of the tube just before the constriction commences.

The connections with the battery wires are made by means of binding screws in such a manner that the current will pass from the vessel, E, to the cell, D; 30 c.c. of dilute sulphuric acid are then poured into E, containing the anode, and 20 c.c. of dilute acid are also run into the cell, D, by means of the stoppered bottle, B, the stem of which must be left full of liquid.

When all the connections are complete and the acid has been added, the current is switched on and the time noted. At the end of 10 minutes, the apparatus is practically free from air, and the issuing

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hydrogen may be lighted. At the same time, the Bunsen burner is lighted and the flame carefully adjusted so that the small piece of platinum gauze is maintained at a red heat throughout the experiment. The heating of the tube during the passing of the gas is continued for 15 minutes, and if, during that time, no brown ring or deposit of arsenic has been formed in the constricted tube (best seen by holding a white card beneath the tube), the apparatus and the acid may be considered free from arsenic and suitable for the application of the Two c.c. of amyl alcohol are then run into the inner cell, D, by test. means of the tap-funnel, B. This is at once followed by the addition of the solution to be tested, prepared as described, 5 c.c. of water being used for rinsing out the containing vessel. No air must be admitted, and the stem of the funnel must be left full of liquid. If arsenic is present in the added liquid, a deposit begins to form in the narrow tube in the course of a few minutes at a point between 1 cm. and 2 cm. from the heated shoulder. At the end of 30 minutes, the whole of the arsenic, except in very extreme cases, will have been deposited in the tube, which is now sealed up while full of hydrogen. This is effected in the following manner. The stopper of the funnel is opened and a small, pointed flame is at once directed against the narrow tube at a point 3 cm. from the deposit, between the deposit and the turned-up end of the tube, which is meanwhile held by a pair The tube at once collapses, and the end is drawn off. of forceps. The electric current is at the same time disconnected, and then the tube is similarly heated and drawn off just below the shoulder. The deposit of arsenic must on no account be heated by the flame during the sealing of the tube. The short tube, about 4 cm. long, containing the arsenic deposit may then be mounted on white card for reference.

Of course, if the deposit of arsenic thus obtained should be so considerable as to prevent accurate comparison with the standard deposits, the experiment must be repeated upon a smaller quantity of the substance.

Preparation of the Standard Deposits.—Although there is good reason to believe that the amount of arsenic deposited is in nowise affected by the nature of the substance with which the arsenic may be associated—0.01 mgm. of arsenic in beer, for example, giving a deposit of equal intensity with the same quantity of arsenic in malt—nevertheless, as the quantitative estimation is based on comparison, it is expedient to make use of deposits prepared by the addition of known amounts of arsenic to arsenic-free specimens of each class of substance. By so proceeding, all doubts which may arise from differences in the nature and composition of the substances on the formation of the deposit are obviated. Thus, for example, in the case of hops and malt, although the final solution to be tested is substantially an acid solution of alkaline earths containing a minute quantity of arsenic, nevertheless, as the malt and hops behave somewhat differently on incineration, and themselves contain different amounts of inorganic matter, it is advisable to make the standards by which malt and hops are to be compared directly from these substances.

The preparation of a solution of arsenic of definite strength for this purpose must be carefully carried out. Pure, resublimed arsenious oxide is ground to a fine powder in an agate mortar and dried at 100°. 0.1 gram is accurately weighed on a watch glass and transferred to a litre flask by washing it down a funnel placed in the neck of the flask with 1 or 2 c.c. of pure concentrated hydrochloric acid. The liquid must not be heated. When the solution is complete, it is diluted to 1 litre with distilled water and thoroughly mixed. Each cubic centimetre of this solution (conveniently called A) contains 0.0001 gram, or 0.1 mgm. of arsenious oxide. Of this solution, 100 c.c. are carefully measured and transferred to another litre flask and diluted with water to 1 litre. This solution (conveniently called B) contains in each c.c. 0.00001 gram (0.01 mgm.) of arsenious oxide.

*Malt.*—It is first necessary to obtain a malt free from arsenic. In certain of the experiments, malt of this character was obtained by drying green malt by means of steam heat. In others, a malt was used which had been dried in cylinders and out of contact with the fumes of fuel. The absence of arsenic in the reagents to be employed must also be ascertained by carrying out a control experiment with the malt, in all respects similar to the actual experiment, but without the addition of arsenic.

Ten grams of arsenic-free malt, previously ground in a mortar, are placed in a porcelain, or preferably a platinum, dish, and 0.2 c.c. of standard arsenic solution *B*, containing 0.002 mgm. of arsenious oxide, is added from a sufficiently narrow burette.\* The whole is then treated in the manner described in connection with the examination of malt, by the basic method. Similar deposits are obtained for 0.004, 0.006, 0.008, 0.010, 0.012, 0.014, 0.016, and 0.018 mgm. respectively.

Hops and Hop Substitutes.—A similar series of standards for hops and hop substitutes is prepared by taking 5 grams of hops, previously ascertained to be free from arsenic, adding definite amounts of the standard arsenic solution, and carrying out the method of examination as described in connection with hops.

Wort and Beer.—A series of standards is prepared for each of these by adding to 25 c.c. of the measured liquid definite amounts of the

\* The burette used in the experiments had an internal diameter of 7 mm., and 1 cubic centimetre occupied a length of 20 mm.

standard arsenic solution B, the liquid being treated in the manner described in connection with the test for wort and beer.

A series of standard deposits is also made for each of the following groups of substances—malt substitutes (glucose and invert sugar), yeast and yeast foods, and chemicals.

Fuel.—With regard to the standards for fuel, it has been shown by direct experiments (v. "The Estimation of Arsenic in Fuel," p. 969) that all the arsenic which may be present in fuel is obtained by the method described, partly in the hydrochloric acid distillate from the solution of the ash, and partly in the solution containing the arsenic volatilised during combustion; and the amount of arsenic in fuel may be accurately estimated by a comparison of the arsenic deposits obtained by testing the fuel in the prescribed manner with the standards employed in the case of chemicals.

The following table gives the amounts of arsenic, represented by the various standard deposits, converted into grains per pound, or per gallon, or per cwt., according to the nature and amount of the substance tested. In the case of malt, the amount of arsenic in grains per pound is converted into its equivalent in grains per gallon of beer on the assumption that a gallon of beer of the standard gravity 1.055 is produced from  $2\frac{1}{3}$ lbs. of malt.

Arsenic deposits obtained from						
Standard As <sub>4</sub> O <sub>6</sub> solution.	10 grams of malt.		25 c.c. of wort, beer, or other liquid.	5 grams of hops, sugar, caramel, yeast, or other substance.	1 gram of chemicals.	10 grams of fuel or sulphur.
Mgm.	Grains per 1b.	Equal to grains per gallon of beer.	Grains per gallon.	Grains per lb.	Grains per lb.	Grains per cwt.
$\begin{array}{c} 0.002\\ 0.004\\ 0.006\\ 0.008\\ 0.010\\ 0.012\\ 0.014\\ 0.016\\ 0.018\\ \end{array}$	$\begin{array}{c} 7 & \frac{1}{2} & \overline{0} \\ 3 & \overline{0} & \overline{0} \\ \hline 2 & \overline{4} & \overline{0} \\ \hline 1 & \overline{1} & \overline{1} & \overline{1} \\ \hline 1 & \overline{1} & \overline{1} & \overline{1} \\ \hline 1 & \overline{1} & \overline{2} & \overline{0} \\ \hline 1 & \overline{1} & \overline{1} & \overline{1} \\ \hline 1 & \overline{1} & \overline{0} & \overline{1} \\ \hline 1 & \overline{0} & \overline{0} \\ \hline 1 & \overline{1} & \overline{1} & \overline{0} \\ \hline 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ \hline 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ \hline 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ \hline 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ \hline 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1 & \overline{1} & \overline{1} & \overline{1} & \overline{1} \\ 1$	309 1513 1514 1514 100 177 77 107 107 107 107 107 107 107	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	10 10 10 10 10 10 10 10 10 10 10 10 10 1	יין דיין דיין דיין דיין דיין דיין דיין	$\begin{array}{c} 0.15 \\ 0.31 \\ 0.46 \\ 0.62 \\ 0.77 \\ 0.93 \\ 1.09 \\ 1.24 \\ 1.40 \end{array}$

The advantages of the electrolytic method are: 1. That it obviates the use of zinc. VOL. LXXXIII.

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2. It is simple in execution, is under perfect control, and may be carried out under such conditions that the results obtained by different operators are strictly comparable, inasmuch as with a current-strength of fair regularity the evolution of the gas is practically constant and uniform.

3. The whole of the solution to be tested for arsenic may be added to the apparatus at once, so that during the whole time of testing the arsenic is under the influence of the "nascent" hydrogen.

4. It has been established that such amounts of arsenic as are present in beer or its ingredients are evolved as hydrogen arsenide during the 30 minutes occupied by the test. The nature of the material associated with the arsenic is found to exercise no inhibiting effect on the formation and evolution of the hydrogen arsenide. Aqueous extracts of malts and worts may be added directly to the electrolytic apparatus without previous destruction of the organic matter as required by the zinc and acid process.

5. The deposits obtained are more uniform in character than those furnished by the zinc and acid method, and admit therefore of more accurate quantitative comparison.

6. The process allows of the simultaneous execution of a number of estimations of arsenic, depending on the arrangement of the rheostat.

The disadvantages of the methods are :

1. The initial cost of the apparatus as compared with that employed in the zinc and acid method.

2. That it can only be applied when an electric current of sufficient intensity is available.

I desire to acknowledge the great assistance I have received from Mr. George Stubbs in working out the details of the method described in this communication.

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