

SUMMARY.

(1) The volatile oil obtained by steam distillation of the alcoholic extract had a phenol content of 89 p. c.

(2) The presence of formaldehyde and acetaldehyde in the aqueous cohobate is indicated.

(3) The non-saponifiable material from the petroleum-ether extract was found to contain a considerable amount of thymol. If this amount of thymol is added to that in the volatile oil, the percentage is found to be 1.3 p. c., which is a surprisingly large yield.

(4) Linolenic, oleic and possibly palmitic acids were found to be present in the saponifiable portion of the petroleum ether extract.

(5) Hydrothymoquinone was identified and a glucoside of hydrothymoquinone was indicated in the water-soluble portion of the alcoholic extract.

THE USE OF ALUMINUM AND STANNOUS CHLORIDE IN THE
GUTZEIT TEST FOR ARSENIC.*

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Analytical chemists have encountered two major difficulties in the detection of small amounts of arsenic by the Gutzeit and Marsh Methods. These obstacles are *first*, arsenic-testing zinc varies markedly in its purity, and *second*, it is very difficult to obtain this metal in a strictly arsenic-free state. Of these, the former is more conducive to poor results than the latter.

The zinc that is to be used for the evolution of hydrogen in these tests is not easily produced in an arsenic-free condition. The results of experiments indicate that some of the drillings from various sections of a supposedly arsenic-free zinc slab contain arsenic, whereas similar drillings from other sections of the same slab do not. The apparent variation in the arsenic contents throughout the zinc slab may be due as much to the difference in formation of active (*i. e.*, atomic) hydrogen caused by an uneven distribution of metallic impurities as to the irregularity in arsenic contents.

The purity of a metal plays a very important part in the rate of formation of active hydrogen. The rate of formation of active hydrogen is in turn an important factor in the reduction of a substance. In the Gutzeit and Marsh tests very small amounts of arsenic are usually dealt with. Unless a certain reducing action exists during the arsenic-testing reaction, the arsenic present may not be entirely reduced to arsine (AsH_3). That is to say, it appears that it is difficult to displace the last traces of arsenic introduced into the reaction.

The metals which occur below hydrogen in the potential series are capable of causing an evolution of hydrogen when introduced under suitable conditions into a dilute solution of an ionizable acid. The velocity of the reaction varies to a marked extent with the purity of the metal. Pure zinc, for instance, is almost unattacked by pure dilute sulphuric acid, but if the zinc be touched with a copper rod below the surface of the acid, solution of the zinc at once commences with

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copious evolution of hydrogen. The resulting hydrogen bubbles are actually evolved from the copper rod, not from the zinc itself, although it is the zinc and not the copper which is passing into solution. A short-circuited cell (Fig. 1) is produced, and the production of such a cell is the cause of the rapid attack (1).

Instead of touching the zinc with a copper rod, the violent reaction of pure zinc with the acid can be brought about by adding a trace of copper sulphate to the acid. At once metallic copper is deposited on the surface of the zinc. Short circuited cells or "couples" of the type just described are formed all over the surface, and the rate of attack by the acid becomes very violent.

If zinc is impure, the "couples" may be formed upon the surface even without the addition of copper sulphate or similar salt to the solution. If the zinc contains a mere trace of a comparatively noble metal, such as copper, nickel, gold or platinum, the rate of attack by acid is notably increased. The attack of acid upon slightly impure zinc often is not very rapid when the metal is first immersed in the acid, because the small amount of impurity may exist in solid solution in the zinc and will not therefore constitute the cathodic element of a couple at the moment of immersion. The slow action, however, brings a certain amount of the noble metal into solution and it is then reprecipitated, as a separate phase, upon the surface

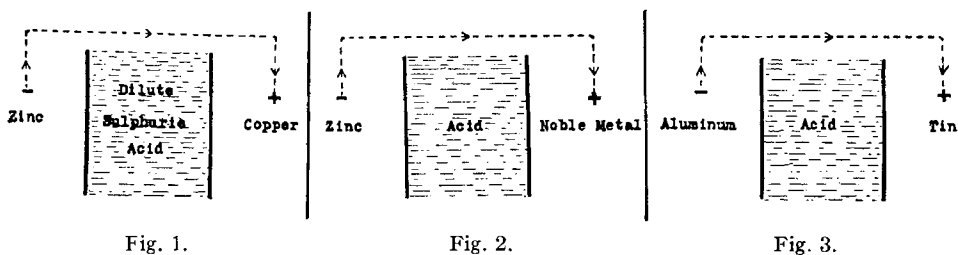


Fig. 1.

Fig. 2.

Fig. 3.

of the metallic zinc. As soon as this occurs, the couple (Fig. 2) appears, and the attack by the acid becomes very much quicker (1).

Since arsenic-testing-zinc varies markedly in purity, a wide variation in the amount of active hydrogen formed over a certain period of time will result by the treatment of different zinc samples with the same concentration of acid. As explained, the rate at which active hydrogen is produced by zinc and a definite concentration of acid varies inversely as the purity of the metal. In other words, the purer the zinc the more slowly will hydrogen be evolved, whereas the larger the percentage of impurities in the metal the more rapidly will hydrogen be produced. Therefore, a very impure zinc will cause a violent evolution of hydrogen, even if the arsenic-testing-apparatus is cooled. Hence, any arsine resulting therefrom will give rise to a "spreading" of the arsenic stain on the mercuric bromide paper in the Gutzeit apparatus. This condition makes an accurate comparison between different stains very difficult. Therefore, it will be noted that the quantity and also the uniformity of flow of hydrogen are important factors in arsenic determination by the Gutzeit Method.

The better grades of commercial aluminum are uniform in purity, varying only between 99 and 99.5 per cent of aluminum. This fact alone gives aluminum a decided advantage over zinc. Uniformity of reactions in arsenic-testing is assured by the use of different samples of the better grades of aluminum.

The minerals cryolite, $\text{AlF}_3 \cdot 3\text{NaF}$, and bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, now used in the Hall-Herault electrolytic production of aluminum, are said to be arsenic-free. Due to the nature of the Hall-Herault process there is no possibility of introducing arsenic during the fabrication of aluminum. As a result, this metal is easily obtained in an arsenic-free condition, a fact that has been proven experimentally.

Because a small amount of aluminum gives a good flow of hydrogen over a long period of time, only small quantities of the metal and acid are required for the arsenic tests. By using a small amount of these reagents the danger of introducing arsenic is again reduced.

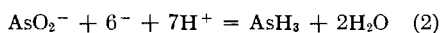
During the first ten or fifteen minutes of a test, aluminum reacting with concentrated hydrochloric acid produces a desirable flow of hydrogen. However, the reaction subsequently becomes too violent. On the other hand, a less concentrated hydrochloric acid will not give the required flow of hydrogen for some time.

When making use of the aluminum-hydrochloric acid reaction only part of the arsenic present in a sample will be shown by the Gutzeit test. Similar but less marked results also will be obtained by using a very pure zinc. The reducing power of active hydrogen varies in proportion to the rate at which it is formed.

In order to stimulate the production of active hydrogen from aluminum, a number of salts of noble metals were tried. Stannous chloride was found to be very well adapted to this purpose. Upon its introduction, in a sufficient amount, into the aluminum-dilute hydrochloric acid mixture, the tin is precipitated and an aluminum-tin couple immediately forms. A steady production of active hydrogen is at once obtained and maintained during the entire time of the arsenic test. All of the arsenic introduced into such a reaction is entirely displaced.

In the presence of the aluminum-tin couple, active hydrogen is formed upon the surface of the tin instead of upon the surface of the aluminum. The aluminum dissolves and the tin remains in the metallic state, thus acting as a catalyst. Inasmuch as the better grades of commercial aluminum are very pure and of a consistent degree of purity, an equal formation of active hydrogen is assured at all times when adding a constant amount of stannous chloride to the aluminum-acid reaction. In this way, the difficulties arising from the use of metals, such as zinc, which contain variable amounts of metallic impurities, are eliminated.

Over the reducing effect of the hydrogen produced by the action of aluminum and acid there is also the cathodic reduction brought about by the formation of the aluminum-tin couple or short-circuited cell (Fig. 3). Aluminum and tin are fairly far apart in the electromotive series of the metals, so that an appreciable electromotive force is set up between them during the reaction. We may attribute the complete displacement of arsenic during the aluminum-tin hydrochloric acid reaction to this added cathodic reduction:



W. E. Lawson and W. O. Scott (3) proposed an electrolytic modification of the Gutzeit Method for the determination of arsenic in body tissues. An electrolytic apparatus, with a current of 0.9 ampere at 5 volts, was used by these authors.

METHOD.

The Gutzeit Method in which aluminum and stannous chloride were used is as follows:

One gram of aluminum granular powder (about No. 20 mesh) is placed in the reduction bottle of the apparatus. Fifty (50) cc. of 5 per cent hydrochloric acid, containing 0.8 cc. of acid-stannous-chloride solution¹ are added. The solution to be tested is then introduced into the bottle and the stopper holding the exit tubes immediately inserted. The apparatus is placed in cold water in order to maintain a uniform temperature and a steady evolution of hydrogen. The reaction is allowed to proceed for one hour.

DISCUSSION.

This test is fundamentally the same as that of the U. S. P. X, with the exception that one Gm. of aluminum replaces 8 to 10 Gm. of zinc, and that 50 cc. of 5 per cent hydrochloric acid are used instead of 25 cc. of 20 per cent sulphuric acid. Eight-tenths of a cc. (0.8 cc.) of acid-stannous chloride is added instead of the 5 drops (0.25 cc.) prescribed in the U. S. P. X.

The apparatus is the same as that designated by the U. S. P. X, with the exception that a 100-cc. reduction bottle should be employed in place of the one of 50 cc. capacity.

The addition of the specified amount of stannous chloride is absolutely necessary. By using smaller quantities, or by its omission, the required formation of active hydrogen will not be obtained and the aluminum method of testing for arsenic will not give consistent results.

The aluminum must be in a uniform granular or so-called "powdered" form. If larger irregular pieces of the metal are used the production of active hydrogen will not be uniform because the tin may form a couple with the smaller particles only. This would lead to variable results.

The stains obtained by the aluminum-stannous-chloride method compare very favorably with those obtained when zinc is used. They are more regular, longer and somewhat more intense. One-half of a micro-milligram of As_2O_3 (equal to 0.4 micro-milligram of As^2) gives an appreciable yellow band with the aluminum-stannous-chloride test.

C. R. Sanger and O. F. Black (4) developed a quantitative determination of arsenic by the Gutzeit Method in which one micro-milligram of As_2O_3 is set as the practical limit of delicacy. By treating their arsenic stains with hydrochloric acid they were able to increase the length and intensify the color of the stains. The sensitized mercuric paper used had a width of 4 mm. Smaller amounts of arsenic, as little as 0.08 micro-milligram of As_2O_3 , could be detected by using 2-mm. bands and by a subsequent development with reagents such as hydrochloric acid, ammonia or auric chloride.

Three grams of uniformly granulated zinc and 15 cc. of dilute hydrochloric acid (1:6) were used by Sanger and Black to generate hydrogen.

In the method herein introduced the successful substitution of aluminum for zinc is the main concern.

Mercuric bromide paper of 3-mm. width, as prescribed by the U. S. P. X, was used in the present experiments. Relative to the delicacy of the introduced method

¹ Acid-stannous chloride is prepared by dissolving 40 Gm. of stannous chloride in 60 cc. of concentrated hydrochloric acid.

² $197.9 \text{ Gm. } As_2O_3 = 149.9 \text{ Gm. } As; 0.000005 \text{ Gm. } As_2O_3 = 0.00000378 \text{ Gm. } As.$

it may be said to compare favorably, under the same conditions, with Gutzeit tests in which zinc is employed.

EXPERIMENTAL PART.

Table I. Gutzeit Tests with Aluminum and Stannous Chloride.—The following are part of the experiments performed in connection with this work where the time of the reaction, the amount of aluminum granules, the quantity and strength of acid and the amount of stannous-chloride-acid solution are at or near the right proportions. These experiments serve to compare the length and color of stains using varying amounts of stannous-chloride-acid solution and of arsenic trioxide.

Time, hours.	Metal Al granules, Gm.	Acid HCl—50 cc. per cent.	Amount of SnCl ₂ acid solution ¹ cc.	Amount of As ₂ O ₃ ² in mmgm.	Length mm. and color of stain.
1½	2	4	0.4
3	1	4	0.4	1.0	3, light yellow
1½	1	4	0.4	2.0	4, deep yellow
1½	1	5	0.6	1.0	6, yellow
1½	1	5	0.6	2.0	7, deep yellow
1½	1	5	0.6	3.0	10, orange
1½	1	5	0.7	0.5	3, yellow
1½	1	5	0.7	1.0	4, yellow
1½	1	5	0.7	2.0	10, lemon yellow
1½	1	5	0.7	3.0	10, orange
1½	1	5	0.7	4.0	20, orange
1½	1	5	0.8	2.0	10, orange

¹ See note page 640.

² Solution of As₂O₃ prepared as directed by U. S. P. X.

Table II. Experiments Showing Necessity of Adding Stannous Chloride to Aluminum in Order to Entirely Displace the Arsenic Introduced.—No reduction of the arsenic takes place in the absence of stannous chloride. Upon its addition in a sufficient quantity, however, reduction immediately proceeds and the arsenic is displaced entirely.

Time, hours.	Metal Al granules.	Acid HCl.	Amount of SnCl ₂ acid solution.	Amount of As ₂ O ₃ in mmgm.	Length mm. and color of stain.
1½	1 Gm.	50 cc. 4%	2
1½	Same reaction as above + fresh HgBr ₂ strip		+ 0.4 cc. SnCl ₂ sol.	..	3, deep orange

DISCUSSION OF METHOD.

(a) The addition of a sufficient amount of stannous chloride is absolutely necessary in order to displace all of the arsenic introduced into the reaction. Acid-stannous-chloride solution in amounts smaller than 0.7 cc. does not give consistent results.

(b) It is important that the aluminum to be used in arsenic-testing should be in a uniform "granular powder." Thin aluminum turnings, unless reduced to a uniform "granular powder," do not give consistent results. Thin polished aluminum sheets, although cut into small uniform pieces, do not give satisfactory arsenic-testing reactions. This is likely due to the very hard condition of the metal in that form, giving rise to a slow and uneven formation of the aluminum-tin couple.

(c) Careful observation of all the experiments in which the proper amount of aluminum-stannous chloride and hydrochloric acid has been used shows that most of the arsenic introduced into these reactions is displaced within one hour. In other words, a full intensity of the stain is obtained within one hour by the above

reaction. This is also the time required to obtain the full intensity of a stain by the U. S. P. X Method using zinc.

(d) Commercial aluminum "granular powder" contains arsenic. It appears that this arsenic is unintentionally introduced by its manufacturers at the time of granulating or "powdering" the metal. During this process the aluminum likely comes in contact with screens made of other metals that contain arsenic.

(e) A long period of time is required in arsenic-tests using aluminum when adding too small an amount of stannous chloride.

(f) A good arsenic-displacing reaction follows upon the use of one Gm. of aluminum "granular powder," 50 cc. of 5 per cent hydrochloric acid and 0.7 to 0.8 cc. of acid-stannous-chloride solution.

Since stannous chloride plays an important part in the aluminum method, it is recommended that a stannated hydrochloric acid be prepared for use in all of the arsenic tests. This stannated hydrochloric acid may be made by adding 1.6 cc. of acid-stannous-chloride solution to each 100 cc. of the 5 per cent hydrochloric acid. By the use of this stannated acid a uniform amount of stannous chloride will be added to each arsenic test and a greater uniformity of result will be obtained.

It is recommended that the aluminum which is to be used for arsenic-testing be a No. 20 mesh "granular powder." An arsenic-free aluminum (No. 20 mesh), especially suitable for arsenic-testing, can no doubt be made by shaving off transverse sections of aluminum wire having a diameter of approximately one millimeter. In this way, the possibility of arsenic-contamination in the process of reducing aluminum to a powder would be avoided.

Table III. Comparison of Flow of Hydrogen Produced by: (a) Aluminum. (b) Aluminum + stannous chloride. (c) Zinc.

(a) 1.00 Gm. Al gran. No. 20 mesh + 50 cc. 5% HCl. Temp. kept at 20° C.

(b) 1.00 Gm. Al gran. No. 20 mesh + 50 cc. 5% HCl + 0.8 cc. SnCl₂ acid sol. temp. kept at 20° C.

(c) 9.00 Gm. Zn pellets + 25 cc. 20% H₂SO₄ + 0.25 cc. SnCl₂ acid sol. temp. kept at 20° C.

Time, minutes.	(a) Vol. of H ₂ , liters.	(b) Vol. of H ₂ , liters.	(c) Vol. of H ₂ , liters.
10	3.5	10	5
20	8.0	20	22
30	12.0	32	34
40	17.5	44	46
50	21.5	56	58
60	25.5	66	70
70	29.5	76	82
80	34.0	86	92
90	38.5	96	102

The above are approximate measurements of the flow of hydrogen and serve only a comparative purpose. The apparatus employed consisted of a generating flask with thistle and delivery tubes, a pneumatic trough and one- and two-liter flasks. The generating flask was placed in water kept at 20° C.

The aluminum-stannous-chloride-acid reaction is seen to give as uniform a flow of hydrogen as in the method in which zinc is used. The catalytic effect of stannous chloride on aluminum during the reaction is clearly shown by the difference in the flow of hydrogen in (a) and (b).

GENERAL CONCLUSION.

The aluminum-stannous-chloride-hydrochloric-acid reaction has very good possibilities as a substitute for the zinc-sulphuric acid reaction in the Gutzeit test in that many difficulties met with in arsenic-testing by the present zinc-procedure are eliminated.

The Dutch Pharmacopœia V (5) has a Gutzeit arsenic-testing procedure in which is directed a method somewhat similar to that developed in this work. However, 0.2 Gm. of aluminum or 0.5 Gm. of zinc and 3 cc. of a one per cent acid-stannous-chloride solution are used in the Dutch Pharmacopœia. This method is claimed to detect one micro-milligram of arsenic (As). A much smaller amount (0.4 micro-milligram) is detectable by the method herein dealt with. It will be noted that the amount of stannous chloride used by the Dutch Pharmacopœia is much less in proportion to that employed in the method recommended. Because of the insufficient amount of stannous chloride used, the Dutch Pharmacopœial method, although using aluminum, is not likely to be as delicate as the method of procedure herein described.

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THE ULTRAVIOLET TRANSMISSION OF LIQUIDS.

BY ELLERY H. HARVEY.

(Concluded from the November 1930, number.)

QUANTITATIVE DISTRIBUTION OF THE LIGHT.

Range Å.	Per cent total radiation.
3020 to 3600	2.0
3600 to 4800	18.5
4800 to 6000	9.3
6000 to 14000	16.5
14000 to 42000	22.1
42000 to 120000	31.6

Since the wave-lengths of the source of light approximate rather closely those received from the sun, and the intensity of the former is 4700 foot-candles while a bright Chicago day between the hours of 12 noon and 2 P.M. registers slightly in excess of 4000 foot-candles, the results reported may be considered somewhat comparable to sunlight exposure.

The basis of calculation is the number of milligrams of oxalic acid decomposed in two hours irradiation, using distilled water (or equally transparent media) in the quartz cell as the screen. All determinations gave the same value, *i. e.*, 140.4 mg. Water being transparent to ultraviolet of this wave-length, the value of 140.4 mg. was taken as 100% transmission and all results obtained calculated to