would be increased by adding one-twentieth or one-thirtieth to the amount of titanic acid found under the conditions that we have used.

The great influence of the action of air is shown by two determinations which were made exactly like those given in the above table, except that, after cooling in carbon dioxide, the solutions were transferred to beakers and titrated as quickly as possible.

Potassium titanofluoride taken	Titanium Found.	Titanium calculated.	Error.
0.6831	0.1078	0.1366	0.0288
0.9545	0.1535	0.1909	0.0374

The volumetric method, even without correction, will be likely to give more reliable results than those obtained by gravimetric determination, unless great care and skill are displayed in carrying out the latter.

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ARSENIC IN GLYCEROL.

BY G. E. BARTON.

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IN following up the literature of glycerol I find that the first to note the presence of arsenic in the medicinal article was Jahns,[2] but he apparently did not investigate the subject thoroughly.

E. Ritsert[3] was the next to take the subject up. He showed the presence of arsenic in seven samples of medicinal glycerol, by the following test, which he says shows 0.001 mg. in one cc. while the Marsh test shows only 0.01 mg. in one cc. One cc. of glycerol is placed in a small measuring cylinder and to this one cc. of water is added, together with fifteen drops of hydrochloric acid and 0.6 gram zinc. The top of the cylinder is covered with filter-paper, moistened with a 1 : 1 silver nitrate solution or saturated mercuric chloride solution, and a yellow stain is obtained on the paper if arsenic is present. Ritsert also states that ammoniacal silver nitrate solution is a good reagent for arsenious acid and that the arsenious acid present probably

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[1] Read at the Springfield Meeting.

[2] Pharm. Ztg., *1888*, 652.

[3] Pharm. Ztg., *1888*, 715, and *1889*, 104, 360 and 625.

explains the difference in the indications given by litmus and phenolphthalein as observed by him. He gives as the probable source of the arsenic found, the sulphuric acid used in the course of manufacture. Issue is taken with G. B. Smith,[1] who states that glycerol itself reduces silver nitrate, and hence ammoniosilver nitrate can not be used to detect arsenic.

An abstract of an article by G. Vulpius[2] gives the cost of an article free from arsenic as ten per cent. more than the current price.

L. Siebold[3] on "Arsenic in Glycerol," finds from one in 4000 to one in 6000 parts of arsenious acid in glycerol used for perfuming and medicinal purposes, and in one case one part in 2500 parts. All glycerols free from arsenic were traced to one process described as that "by which as a rule glycerol used for dispensing purposes is understood to be made." He ascribes the presence of arsenic in some cases to the solution of the arsenic present in the glass of the bottle, but this has never been confirmed and hardly seems probable.

Dr. Benno Jaffé[4] attacks the ammonio silver nitrate test which he claims to be of no value as it does not give constant results, either for arsenic or acrolein and similar bodies.

J. Luttké,[5] after an elaborate examination of twenty-one samples confirms Jaffé's conclusions and points out as among the disturbing causes, chlorides and organic acids.

There can be no doubt of the presence of arsenic in some glycerol, but I have found no one except Siebold who has attempted to give any idea of the quantity, and while he does not give the method used in obtaining the results stated, I infer from the text that, using either silver nitrate or mercuric chloride to absorb the hydrogen arsenide, he has compared the depth of color obtained with that given by known quantities of arsenious acid. A few experiments led me to think that this cannot be a very accurate method at best, so I set about to apply the method given by Sanger, for the estimation of arsenic in wall paper[6] which

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[1] Ned. Tijschr. v. Pharm., *1889*, 143.

[2] Apoth. Zeit., *1889*, 4. 439; *J. Soc. Chem. Ind.*, 8, 639.

[3] Pharm. J. Trans. [3], 20, 205.

[4] Chem. Ztg., *1890*, 14, 1493.

[5] Apoth. Ztg., *1891*, 6, 263.

[6] Proc. Amer. Acad., 26, 24.

consists of comparing the mirrors obtained in a modified form of the Marsh apparatus with those prepared from known quantities of arsenious oxide in solution as sodium arsenite.

The apparatus as described by Sanger consists of a constant hydrogen generator, filled with chemically pure sulphuric acid and zinc, a smaller reduction flask having a thistle tube for introducing acid and solutions to be treated and which of course contains a small amount of chemically pure acid and zinc, a drying tube containing calcium chloride, and finally a reduction tube in which the mirror is obtained.

The cost of using chemically pure acid and zinc in the constant hydrogen generator would of course be great, and the first point I turned my attention to was a method for purifying the hydrogen generated by impure acid and zinc so that the constant generator could be run at a reasonable cost. I found that by passing the hydrogen through silver nitrate solution, the arsenic was removed entirely, according to the well-known reaction:

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 3Ag_2.$$

Another improvement in the apparatus as I used it was the substitution of a small separating funnel for the thistle tube in the reduction flask. This prevented the escape of any gas at that point while the former arrangement allowed a variable quantity to escape.

The apparatus as finally used in this work, consisted of a constant hydrogen generator, using impure acid and zinc, a wash bottle containing silver nitrate solution, a wash bottle containing water to remove any traces of silver nitrate solution which the gas might carry mechanically and which would otherwise hold back some of the arsenic in the reduction flask, a reduction flask, with separating funnel as before described, a drying tube containing calcium chloride, and finally the reduction tube.

The efficiency of the silver nitrate solution was proven by running over one hundred hours without obtaining a mirror, whereas a mirror could be obtained in from five to ten minutes from the same hydrogen not passed through silver nitrate. Using the ordinary acid and zinc of the laboratory, I found an amount of silver nitrate solution representing one gram of the salt prevented the formation of a mirror for over two hundred hours.

The mode of operating did not differ essentially from that described by Sanger. The apparatus was first filled with hydrogen, the reduction flask containing at this time only the pure zinc, of which about three grams were used. The jet at the end of the reduction tube was then lit and the tube heated at the proper place, after which a little sulphuric acid was introduced into the reduction flask and the action allowed to go on for a few minutes to prove the purity of the reagents. The solution to be treated was then added and washed in by more acid, or water where the glycerol was added directly to the flask.

The acid used was about one to eight and by slightly varying these proportions it was found possible to get along without cooling the flask. No two samples of zinc were found to contain the same amount of carbon or at least to dissolve with the same rapidity so that a careful adjustment of the acid is necessary for each lot and as large an amount as possible should be granulated at one time. It is also necessary to have standard mirrors made at different speeds to counterbalance the slight differences which are unavoidable.

The calcium chloride tube should be carefully looked after in order that the gas may be perfectly dry. I have found it best to ignite the article furnished by the makers before using. It is also a good plan to attach the bellows and blow through it a few moments after filling, to remove any slight amount of dust that might otherwise be carried into the reduction tube.

The glass used for the reduction tube should be of the hardest obtainable. I have found great variations in different pieces of the same lot. It would be of advantage if glass were carefully selected, and if necessary carefully tested, could be quoted by dealers, as otherwise a large amount of tubing is accumulated too hard for ordinary work but not hard enough for this purpose. Great care should always be taken to get tubes uniform at the point of deposition and in spite of this it was found necessary to have several mirrors of each grade.

A small white mirror was found to form beyond the arsenic mirror in those tubes representing small amounts but in those obtained from larger amounts either wholly or partly coinciding. In the latter case the arsenic mirror took on a totally different color, the characteristic brown of the pure arsenic mirror becoming black. This mirror was without doubt in some cases partly due to moisture, and showed minute drops when examined under a lens. It also seemed to be less with the harder glasses. After having used fresh calcium chloride and the hardest glass obtainable, the only resource is in having standard mirrors representing all possible variations.

Another trouble was found to be the deposition of the arsenic in two mirrors entirely apart. This Gooch and Moseley[1] suggest to be due to the formation of two allotropic forms of arsenic by the too high heating of the reduction tube. They avoid this by enclosing the reduction tube in an iron or nickel jacket. Here again several mirrors of each standard amount are a remedy.

Having obtained a sufficient number of standard mirrors eight samples of glycerol, such as is ordinarily sold by the druggists of this city were procured. Six represented the best American makers and two were imported.

Five grams of each sample were treated with five cc. of a mixture of thirty parts sulphuric acid and one part nitric acid and the mixture heated carefully with constant stirring till a dry charred mass giving off sulphur dioxide was obtained. This was then allowed to cool and about ten cc. of water added and then the mass again heated till sulphur dioxide was given off. After cooling about fifteen cc. of water was added and the mixture boiled vigorously to expel sulphur dioxide. The liquid was then filtered off and water added as before, boiled and again filtered. This was repeated twice to insure the complete extraction of the arsenic from the charred mass. The solution thus obtained was added to the reduction flask and the usual process carried out. Five of the eight samples showed arsenic in variable amounts.

To prove that arsenic, if present, would be shown by this course of manipulation, five grams of glycerol showing no arsenic were weighed out and one cc. of an arsenic solution added. This mixture was treated exactly as the other samples had been and no arsenic mirror obtained. From this and the comparison

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[1] Am. J. Sci., 48, 294.

of these mirrors with those obtained by other processes, I concluded that some, at least of the samples contain, or are decomposed into something capable of holding black arsenic. This leads to the query: What is the effect of the combined glycerol present in the toxicological examination for arsenic? May not the trouble with the glycerol be due to a decomposition product which would also be formed in the supposed case? I have not had time to investigate this important point.

Five grams of the same glycerol used in the previous experiment were then added direct to the reduction flask after diluting with water and arsenic in small quantities was obtained. One cc. of the arsenic solution was then added to the glycerol and, after diluting, the reduction carried out at once as in the previous experiment and an amount of arsenic equal to that in the one cc. of solution and five grams of glycerol, obtained. After trying several plans this method was finally chosen as both the quickest and most accurate.

The following quantities of arsenious oxide (As_2O_3) were obtained in the eight samples:

No.		No.	
1	trace.	5	faint trace.
2	0.08 mg.	6	trace.
3	faint trace.	7	0.004 mg.
4	none.	8	0.003 mg.

To prove that the mirrors obtained were due to arsenic and nothing else, mirrors were heated gently and moist hydrogen sulphide passed through them. In this manner part of the arsenic was changed to the yellow sulphide. Some of the gas from the reduction flask was passed into silver nitrate solution and a black precipitate of metallic silver obtained. On carefully neutralizing with ammonium hydroxide a yellow precipitate of silver arsenite, soluble in excess, and also in nitric acid was obtained. The nitric acid solution was precipitated with hydrochloric acid, a clean copper wire added and the solution warmed. A grey coating formed on the copper. Blank experiments showed the reagents to be pure.

From the above there can be no doubt but that arsenic was present in the glycerols examined.

The method mentioned by several authors, namely, diluting the glycerol with an equal volume of water, adding hydrochloric acid and then metallic zinc, and obtaining a yellow coloration on a filter-paper moistened with either silver nitrate solution (1 : 1) or saturated mercuric chloride solution was tried. A twenty-five cc. measuring cylinder was used and the paper fastened tightly over the mouth, the gas escaping at the nose. In this manner using the silver nitrate solution the test was found to be about five times as delicate as the Marsh test used, and a trace of arsenic was found in sample No. 4, which had shown none in the Marsh test. The coloration was not permanent enough, owing to the action of light and other causes to be compared with standards made with permanent coloring-matters. The test with mercuric chloride, carried out in the same way, was not quite as delicate as the Marsh test. It would hardly be possible by comparing with standards to make this a quantitative method as accurate as the Sanger-Berzelius-Marsh test. It is to be noted that sample No. 2, which showed the largest amount, contained 0.08 arsenious oxide or one part in 62500, while Siebold reports as much as one part in 2500 in one case. Seventy mg. is the smallest dose known to have produced death according to Tanner[1] which would be equivalent to the amount in over four liters of glycerol No. 2, or to 150 cc. of Siebold's worst sample. Although arsenic is slowly eliminated from the system, still it would be quite possible by the indiscriminate use of sample No. 2, for some time, to accumulate enough in the system to cause death. Certainly the above figures are worthy of note by persons using glycerol for medicinal purposes.

So-called C. P. glycerol is often recovered from the waste products of the soap manufactories, and in this case the presence of arsenic is accounted for as follows: Starting with arsenical oil of vitriol, the arsenic is changed in the hydrochloric acid still to the chloride, which distils over with the acid. On neutralizing the spent lyes with hydrochloric acid the arsenic remains in the solution and is repeatedly distilled over with the glycerol.

In this connection I may say that I found no hydrochloric acid in this laboratory free from arsenic as shown by the yellow stain in the silver nitrate test, but had no trouble in preparing such

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[1] Memoranda of Poisons, p. 69.

an article from chemically pure sulphuric acid which I had proven to contain no arsenic.

In conclusion I take pleasure in acknowledging my deep indebtedness to Dr. Charles E. Munroe for his many suggestions.

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THE OCCURRENCE OF TRIMETHYLENE GLYCOL AS A BY-PRODUCT IN THE GLYCEROL MANUFACTURE.[1]

BY ARTHUR A. NOYES AND WILLARD H. WATKINS.

Received September 9, 1895.

DURING the past winter our attention was called to an unusual difficulty experienced by one of the soap-making firms in the neighborhood of Boston in obtaining their glycerol of the required commercial gravity. The information furnished in regard to it indicated the presence in the glycerol of some uncommon impurity, and a considerable quantity of the "light stuff" having been generously placed at our disposal by the soap company, we were enabled to investigate it. It was submitted to fractional distillation, first at diminished and then at ordinary pressure, and a liquid boiling between 214° and 217° at 760 mm. pressure was thus separated from it. This liquid was found to have a specific gravity of 1.056 at $\frac{20^\circ}{15^\circ}$, and gave the following results on analysis:

0.2293 gram substance gave 0.3998 gram carbon dioxide and 0.2158 gram water.

	Found.	Calculated for $C_3H_8O_2$.
Carbon	47.52	47.37
Hydrogen	10.46	10.53

The substance is therefore trimethylene glycol, which has a boiling-point of 214° and a specific gravity at $\frac{18^\circ}{0^\circ}$ of 1.0526. The isomeric propylene glycol boils at 188°–189° and has a specific gravity of 1.0403 at $\frac{19.4^\circ}{0^\circ}$. The "light stuff" contained a very considerable proportion, about thirty-eight per cent. of glycol.

The origin of the glycol is a matter of considerable interest. There is little doubt that it was produced by fermentation of the

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[1] Read at the Springfield meeting.