

THE DETERMINATION OF ARSENIC IN GLYCERINE.

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THE presence of arsenic in glycerine is probably, by this time, well known to chemists. Several have described its detection qualitatively. Barton,¹ however, was the first to estimate it quantitatively. Barton's method, which was applied on C. P. glycerines only, consists in the charring of five grams of the glycerine with sulphuric and nitric acids, the production of a mirror in the Marsh apparatus, and the comparison of the mirror so obtained with a standard mirror according to Sanger's method.²

As it is impossible to draw an accurate comparison if the mirrors weigh over 0.06 milligram, a suitable aliquot part of the solution must be taken, in order to obtain a mirror weighing less than this amount. This requires some experimenting on the part of the analyst, which becomes very tedious if the glycerine be high in arsenic.

These considerations led the author to abandon the method and adopt a modification of Polenske's process,³ suitable to the case at hand. The method as described by Polenske is accurate with quantities of arsenic up to four to five milligrams. As in glycerine analysis the amount of arsenic in the portion taken rarely exceeds one milligram, the apparatus may be materially simplified.

For analysis we take fifteen to twenty grams of a crude soap lye glycerine and twenty-five to thirty grams of a saponification or C. P. glycerine. With dilute glycerines an amount is taken which would yield the requisite weight upon evaporation. The weighed sample is made up to 100 cc. with hot water and rinsed into a capacious casserole, containing a mixture of 200 cc. of concentrated nitric acid and twelve cc. concentrated sulphuric acid. Cover and heat gently in the hood until the action starts. Remove the flame and wait until the violence of the reaction is over, then boil down slowly over a low flame until dense fumes of sulphuric acid appear. Raise the heat at the end to expel

¹ This Journal, 17, 883.

² Proc. Am. Acad. Sci., 1897, 26, 24.

³ Chem. Centrbl. (1889), 60, [2], 58.

the last traces of nitric acid. If the concentration has been a slow one (four to five hours) the organic matter will generally be entirely oxidized. If the acid turns brown, however, from the charring of organic matter it is well to boil for some time longer to complete the oxidation. There is no danger of losing any arsenic by this treatment. Cool and dilute to fifty cc.

About forty grams of coarsely granulated zinc are placed in the generating flask of the Marsh apparatus. A 75 to 100 cc. stop-cock funnel pierces the stopper. The escaping gas is passed through a wash-bottle containing a five per cent. lead nitrate solution to remove any hydrogen sulphide and is dried by passing through a calcium chloride tube. A tube of hard glass about ten inches long and with an inside diameter of ten to twelve mm. is heated near one end and drawn out at that point to a tube with a diameter of one to one and a half mm. This section serves to catch the metallic arsenic deposited. Of the large sections the longer is heated by two Bunsen burners. To prevent sagging it is well to protect this part of the tube with a roll of copper gauze wrapped around it. The shorter section at the end of the tube holds a slip of filter-paper moistened with a saturated solution of mercuric chloride. This serves to detect the presence of any hydrogen arsenide which might pass the burners undecomposed.

After making connections ten cc. of twenty per cent. sulphuric acid is run into the flask. When the air has been entirely displaced reuse the solution to be tested into the stop-cock funnel, light the burners and run the solution, drop by drop, on the zinc at such a rate that not more than two bubbles a second pass the lead nitrate wash-bottle.

If the mercuric chloride paper should at any time show a yellowish tint the solution should be run in more slowly. If the size of the mirror shows that a considerable amount of arsenic is present, it is well to add, at the end, a little stannous chloride dissolved in hydrochloric acid. In any case add a few cubic centimeters of dilute acid after the entire solution has been run in to expel hydrogen arsenide remaining in the flask.

The section carrying the mirror is separated by a file and carefully weighed on an assay gold balance within 0.01 milligram. This can be readily done, as the weight of the tube sel-

dom exceeds 300 milligrams. The arsenic is dissolved by dipping the tube into hot dilute nitric acid, and after washing and drying the weight is taken again, the difference being the weight of the arsenic forming the mirror. The zinc and acids used should not form a perceptible mirror after running the apparatus three quarters of an hour. The following results were obtained:

Arsenic taken. Milligrams.	Arsenic found. Milligrams.
0.20	0.17
0.50	0.45
0.75	0.68

Several C. P. glycerines were found to be free from arsenic. Arsenic was found in a majority of saponification glycerines. These averaged about 0.00018 to 0.00030 per cent. A number of crude soap-lye glycerines gave percentages lying between 0.00064 and 0.01.

A very fair idea of the arsenic contents may be gained by Gutzeit's test, using mercuric chloride instead of silver nitrate. Two cc. of glycerine are run into a five-inch test-tube and diluted with four cc. of water; a piece of granulated zinc is added and sufficient hydrochloric acid to just start the reaction. The tube is then quickly closed by a cork whose lower end is covered with a seven cm. filter-paper. The paper is wrapped around the cork so that it rests smoothly against the lower end. This part is moistened with two drops of a saturated solution of mercuric chloride. The hydrogen escapes through the creases between the paper and the tube. The evolution of hydrogen should be fairly brisk but not too violent.

After standing ten minutes the cork and paper are removed. The latter is spread out and examined. A yellow stain in the shape of a circle with a diameter equal to the end of the cork is formed if arsenic were present. With very impure glycerines the color is brown. The papers carrying the stains may be marked and kept as records for future comparisons. The color is fairly permanent. By comparing the yellow stain produced by the glycerine under examination with a series of standards prepared by running the same test on portions of a solution of arsenic (one milligram in 100 cc.), the per cent. of arsenic can be gauged quite accurately after a little practice. The color is quite distinct with 0.01 milligram of arsenic and is still percepti-

ble with 0.0025 milligram. If the latter amount were present in two cc. glycerine (sp. gr. 1.26) the per cent. of arsenic present would be 0.00010 which would be about the limit of delicacy by this test.

Gutzeit's test using silver nitrate was found to be very unsatisfactory. It is very difficult to form any idea as to the amount of arsenic present from the intensity of the color in this case. The silver nitrate is also so easily affected by impurities in the zinc and acid other than arsenic that any conclusion as to the presence of the latter should be drawn with great caution.

In view of the rapidity, delicacy, and accuracy of Gutzeit's test, using mercuric chloride, it is difficult to understand why the more laborious Marsh test should still hold its own as a qualitative test for arsenic.

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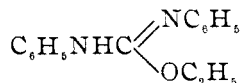
ON THE ISOUREA ETHERS AND OTHER DERIVATIVES OF UREAS.

By F. B. DAINS.

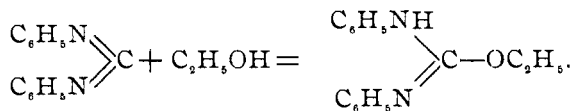
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THE imido ethers, oxygen ethers of ordinary acid amides or anilides, have since their discovery by Pinner in 1883 been exhaustively investigated in many directions on account of their remarkable reactivity.

In 1894, the first representative of the oxygen ethers of a simple urea, ethyl isocarbamilide



was prepared by Lengfeld and Stieglitz.¹ They found that when carbodiphenylimide was heated to 180° in a sealed tube with absolute alcohol, it added the alcohol quantitatively forming ethylisodiphenylurea.



A little later they discovered² that the ethylisodiphenylurea

¹ *Ber. d. chem. Ges.*, 27, 926.

² *Am. Chem. J.*, 17, 112.