

mixtures of these two substances by Tsakalotos<sup>1</sup> and by Thorpe and Rodger<sup>2</sup> lead to the surprising result that the difference  $\Delta v$  (observed specific volume — calculated specific volume) for all examined mixtures is *negativ* and reaches for the equimolecular concentration or thereabout a minimum (after Tsakalotos,  $\Delta v_{18.2^\circ} = -0.015$ , after Thorpe and Rodger,  $\Delta v_{0^\circ} = -0.012$ ) of relatively high value. The case of chloroform-acetone gives also a minimum, though of much smaller values (0.002). It would be highly interesting to extend these determinations of specific gravities, to obtain a good insight into the displacement of this minimum by change of temperature, and to examine whether lowering of the temperature finally leads to a separation of the supposed compound in the solid state. An investigation in this direction by studying the cooling curves of the binary mixtures of *this couple* is planned in this laboratory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UTAH EXPERIMENT STATION.]

### SOME FACTORS INFLUENCING THE QUANTITATIVE DETERMINATION OF ARSENIC IN SOILS.<sup>3</sup>

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Since it has been announced that arsenic occurs in many virgin soils<sup>4</sup> and that it may, on account of its extensive use as an insecticide, accumulate in soils to such an extent as to become injurious to vegetation,<sup>5</sup> the principles involved in its accurate determination are of considerable practical importance at the present time. Many methods, both qualitative and quantitative, have been proposed for its determination in soil, but even the most modern<sup>6</sup> do not make allowance for the influence of the iron in the soil upon the quantitative determination of the arsenic.

That arsenic is retained by iron when the Marsh method is used for its determination was first shown by Parson and Stewart,<sup>7</sup> and later corroborated by the work of Harkins.<sup>8</sup> These investigators found that the arsenic retained by the iron increased as the iron introduced with the

<sup>1</sup> *Z. physik. Chem.*, **74**, 743 (1908).

<sup>2</sup> *Loc cit.*, p. 370.

<sup>3</sup> Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

<sup>4</sup> Headden, *Proc. Colo. Scientific Soc.*, **9**, 349 (1910).

<sup>5</sup> Headden, *Colo. Exp. Sta., Bull.* **131** and **157**.

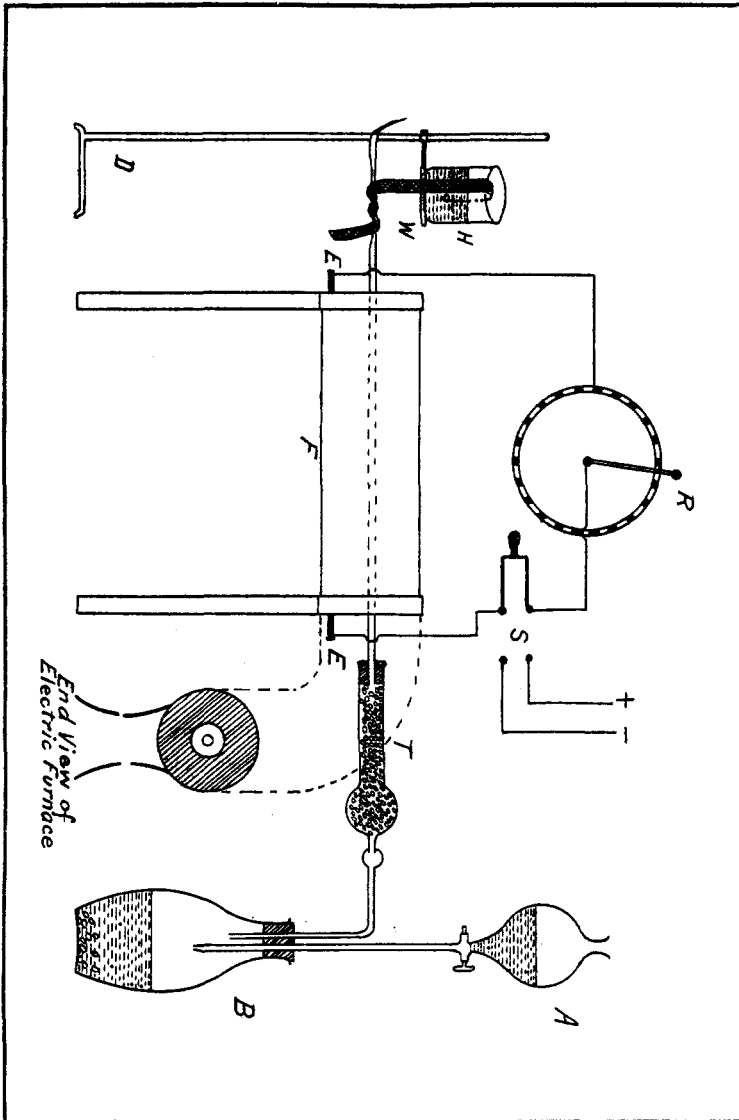
<sup>6</sup> *Mai. Pharm. Centr.*, **50**, 169-200; Headden, *Colo. Sci. Soc.*, **9**, 348 (1910); Haywood, U. S. Dept. of Agr., Bur. of Chem., *Bull.* **113** (revised), 58.

<sup>7</sup> Parson and Stewart, *THIS JOURNAL*, **24**, 1905 (1902).

<sup>8</sup> Harkins, *Ibid.*, **32**, 518 (1910).

arsenic increased. They made tests in which considerable iron was used (6 grams) and found that in some cases only 32% of the arsenic was evolved when introduced into the Marsh apparatus. In their reported work, the smallest amount of iron used was 60 mg. and with even this amount only 69% of the total arsenic was recovered.

In order to determine the influence of traces of iron upon the quantity of arsenic evolved, as with some methods it is recommended that traces of iron be introduced to accelerate the action of the acid upon the zinc,



and to check with the above reported results, I have made tests using varying amounts of iron with constant amounts of arsenic. This was done by introducing a solution of sulfuric acid containing the iron and arsenic into the Marsh apparatus and then determining by weighing on fine assay balances the amount of arsenic deposited. The tube was heated by means of an electric combustion furnace, the temperature of which was maintained just below the melting point of hard glass by means of a rheostat. The constriction in the glass tube where the arsenic was to be deposited was wrapped with a wick dipping into a beaker of cold water (see accompanying figure).

Twenty-five grams of zinc, free from arsenic and iron, were placed in the generator and the acid solution of iron and arsenic was added drop by drop. The sulfuric acid used was the No. 2 (260 cc. pure conc.  $H_2SO_4$ , 1000 cc. of  $H_2O$ ) and No. 3 (425 cc. pure conc.  $H_2SO_4$ , 1000 cc. of  $H_2O$ ) recommended by Chittenden and Donaldson.<sup>1</sup> Acid No. 2 was first used and No. 3 later.

All chemicals before using were tested and found to be free from arsenic. The calcium chloride used in the drying tubes was carefully neutralized, as recommended by Bishop.<sup>2</sup>

The apparatus was allowed to run two hours in each determination. The tube containing the arsenic was carefully wiped with a moist cloth, dried over calcium chloride, a rough weighing made and then allowed to remain in the balance case ten minutes, after which it was carefully weighed, the arsenic was dissolved out by dilute nitric acid (1 to 3), the tube washed in water, alcohol and ether, dried and weighed as before. The tube was handled throughout by means of platinum tipped tweezers, and all possible precautions taken to insure accuracy. Each result reported is the average of two or more closely agreeing determinations.

In Table I is given the amount of arsenic obtained with varying amounts of iron.

TABLE I.—EFFECT OF IRON ON ARSENIC OBTAINED BY MARSH GENERATOR.

Treatment.	Arsenic added. Mg.	Arsenic found. Mg.
Arsenic, no iron.....	1.00	0.98
Arsenic, 1 mg. iron.....	1.00	0.78
Arsenic, 5 mg. iron.....	1.00	0.61
Arsenic, 10 mg. iron.....	1.00	0.58
Arsenic, 50 mg. iron.....	1.00	0.66
Arsenic, 100 mg. iron.....	1.00	0.65
Arsenic, 500 mg. iron.....	1.00	0.33
Arsenic, 1000 mg. iron.....	1.00	0.38

From the above results it may be seen that the arsenic recovered de-

<sup>1</sup> Fresenius, Cohn, *Quantitative Chemical Analysis*, 2, 694 (1906).

<sup>2</sup> Bishop, *THIS JOURNAL*, 28, 182 (1906).

creases very rapidly as the iron added increases. In fact, the amount retained is almost directly proportional to the amount of iron introduced. Even as small an amount as 1 mg. of iron in these tests was sufficient to retain one-fourth of the arsenic, so that even traces of iron must be considered in determining arsenic by the Marsh method.

Harkins suggested that the retaining influence of iron be overcome by the use of stannous chloride and he found that two grams of stannous chloride was sufficient to overcome the retaining effect of three-tenths of a gram of iron. Inasmuch as there would be more than this amount in some soil solutions, it was thought advisable to check on this with varying amounts of iron and stannous chloride. The results are given in Table II:

TABLE II.—THE LIBERATION OF ARSENIC FROM IRON BY MEANS OF STANNOUS CHLORIDE.

Treatment.	Arsenic added. Mg.	Arsenic found. Mg.
1 mg. Fe + 0 mg. SnCl <sub>2</sub> .....	1.00	0.89
1 mg. Fe + 10 mg. SnCl <sub>2</sub> .....	1.00	0.83
1 mg. Fe + 20 mg. SnCl <sub>2</sub> .....	1.00	0.83
1 mg. Fe + 50 mg. SnCl <sub>2</sub> .....	1.00	0.81
1 mg. Fe + 100 mg. SnCl <sub>2</sub> .....	1.00	0.86
1 mg. Fe + 200 mg. SnCl <sub>2</sub> .....	1.00	1.04
1 mg. Fe + 500 mg. SnCl <sub>2</sub> .....	1.00	1.02
5 mg. Fe + 1000 mg. SnCl <sub>2</sub> .....	1.00	0.90
5 mg. Fe + 1000 mg. SnCl <sub>2</sub> .....	1.00	0.97
10 mg. Fe + 1000 mg. SnCl <sub>2</sub> .....	1.00	0.99
50 mg. Fe + 1000 mg. SnCl <sub>2</sub> .....	1.00	1.00
100 mg. Fe + 1000 mg. SnCl <sub>2</sub> .....	1.00	0.99
500 mg. Fe + 1000 mg. SnCl <sub>2</sub> .....	1.00	0.985
1000 mg. Fe + 1000 mg. SnCl <sub>2</sub> .....	1.00	0.65
1000 mg. Fe + 1200 mg. SnCl <sub>2</sub> .....	1.00	0.70
1000 mg. Fe + 1500 mg. SnCl <sub>2</sub> .....	1.00	0.985

From these results it may be seen that the retaining action of one mg. of iron upon the arsenic was offset by 200 mg. of stannous chloride, and that one-half gram of iron was neutralized by one gram of the stannous chloride. One and one-half grams of stannous chloride completely neutralized the retaining influence of one gram of iron upon arsenic.

These facts have been applied to the determination of arsenic in soil. A soil, 40% of which was soluble in hydrochloric acid (sp. gr. 1.115), and containing 2% of iron was analyzed and found to be free from arsenic. To 10 grams of this soil were added one mg. of arsenic and 25 cc. of concentrated nitric acid. The mixture was heated for 30 minutes in a casserole on an electric hot plate and while moderately hot 10 cc. of concentrated sulfuric acid were added drop by drop. When considerable organic matter was present, this caused a violent reaction but no arsenic was lost. This was heated for 30 minutes, taken up with distilled water, filtered and

washed with hot water until free from sulfates. The filtrate was evaporated nearly to dryness or until free from nitrates, the solution being kept strongly acid with sulfuric acid. The residue was taken up with arsenic-free, dilute hydrochloric acid and the arsenic determined in the following manner: In one set the solution was introduced directly into the Marsh generator without further treatment, in another with varying amounts of stannous chloride. Still other determinations were made in which the arsenic was precipitated as the ferro-arsenate by the addition of an excess of ammonium hydroxide as suggested by Headden,<sup>1</sup> and later by Mai.<sup>2</sup> This precipitate was dissolved in hydrochloric acid and one set introduced directly into the generator without further treatment, while other samples were added in connection with varying amounts of stannous chloride. The results are given in Table III:

TABLE III.—AMOUNT OF ARSENIC OBTAINED FROM SOIL CONTAINING 1 MG. ARSENIC WITH VARIOUS METHODS, BOTH WITH AND WITHOUT ADDITION OF STANNOUS CHLORIDE.

Treatment.	Stannous chloride added.	Arsenic added. Mg.	Arsenic found. Mg.
Whole of acid extract.....	0	1.00	0.705
Whole of acid extract, 25 cc. conc. H <sub>2</sub> SO <sub>4</sub> .....	0	1.00	0.82
Whole of acid extract, 25 cc. conc. H <sub>2</sub> SO <sub>4</sub> .....	1.5	1.00	0.95
Whole of acid extract, 25 cc. conc. H <sub>2</sub> SO <sub>4</sub> .....	2.0	1.00	0.96
Excess of NH <sub>4</sub> OH added to soil extract, filtered, residue dissolved in acid.....	0	1.00	0.62
Excess of NH <sub>4</sub> OH added to soil extract, filtered, and dissolved in acid, 25 cc. conc. H <sub>2</sub> SO <sub>4</sub> .....	0	1.00	0.71
Excess of NH <sub>4</sub> OH added to soil extract, filtered, residue dissolved in acid, 25 cc. conc. H <sub>2</sub> SO <sub>4</sub> .....	1.5	1.00	0.87
Excess of NH <sub>4</sub> OH added to soil extract, filtered, residue dissolved in acid, 25 cc. conc. H <sub>2</sub> SO <sub>4</sub> .....	2.0	1.00	0.90
Excess of NH <sub>4</sub> OH added to soil extract, filtered, residue dissolved in acid 25 cc. conc. H <sub>2</sub> SO <sub>4</sub> .....	3.0	1.00	0.88

The 25 cc. of concentrated sulfuric acid referred to in some of the determinations was introduced at the end of the process, that is after the main part of the arsenic had been evolved, but there remained considerable undecomposed zinc in the generator. The introduction of the sulfuric acid at this point in the reaction tends, by increasing the temperature of the solution in the generator, and the rapid evolution of hydrogen, to liberate the arsenic which is retained by the iron. An examination of the above results shows that the addition of the concentrated sulfuric acid at the end of the process gave an increase in the arsenic recovered, except in the cases where the stannous chloride had been used. In these cases there was no increase, probably because all of the arsenic had been liber-

<sup>1</sup> Headden, *Proc. Colo. Sci. Soc.*, 9, 348 (1910).

<sup>2</sup> Mai, *Pharm. Centr.*, 50, 169-200.

ated by the stannous chloride. The addition of 1.5 grams of stannous chloride together with the concentrated sulfuric acid was sufficient to liberate the greater part of the arsenic, as no more arsenic was recovered when the amount of stannous chloride was increased to three grams. Where the arsenic was precipitated with ammonia a smaller proportion of the total arsenic was recovered than when the entire acid solution was introduced into the generator. Even when three grams of stannous chloride were added, it was impossible to recover all of the arsenic added. This is probably due to the slight solubility of the ferro-arsenate.

*Effect of Sodium Chloride.*—The soil used in the above tests contained only 0.0002% of sodium chloride. Inasmuch as the trichloride of arsenic is formed under certain conditions when an arsenic solution is treated with hydrochloric acid and as arsenic trichloride is volatil at a comparatively low temperature, tests were made with a soil containing varying amounts of sodium chloride. Varying quantities of sodium chloride were added to ten grams of soil containing one mg. of arsenic. To these were added 25 cc. of concentrated nitric acid, the mixture was heated thirty minutes, and then 10 cc. of concentrated sulfuric acid added and heated thirty minutes longer, filtered, washed and the arsenic determined as in the preceding work, using 2 grams of stannous chloride. The results are given in tabular form below:

Per cent of NaCl in soil.	Mg. arsenic added.	Mg. arsenic found.
0.0002	1.0	0.955
0.0052	1.0	1.04
0.0102	1.0	0.92
0.0502	1.0	0.98
0.1002	1.0	0.95
0.5002	1.0	0.91
1.0002	1.0	1.01
1.5002	1.0	0.93
2.0002	1.0	0.96
2.5002	1.0	0.97
3.0002	1.0	0.94

From the above results it may be seen that no appreciable quantity of arsenic is lost by this method even when the percentage of sodium chloride in the soil reaches 3%. The results of Chittenden and Donaldson,<sup>1</sup> on the other hand, show that there would be no loss even when large amounts of organic matter are present.

The method, therefore, which has given the best results in the preceding work, is briefly summarized as follows: Ten grams of soil were weighed into a casserol; to this were added 25 cc. of concentrated arsenic-free nitric acid and the mixture heated on a hot plate for 30 minutes. While still moderately hot there was added 10 cc. of concen-

<sup>1</sup> Chittenden and Donaldson, *Am. Chem. J.*, 11, 235.

trated sulfuric acid and the whole heated for 30 minutes longer. The soil was taken up and thoroughly washed with hot distilled water, the filtrate evaporated to dryness, and heated until free from nitrates. The residue was treated with dilute, arsenic-free sulfuric acid to which was added 20 cc. of stannous chloride solution, 1 cc. of which contained one-tenth of a gram of stannous chloride. This solution was slowly introduced into a Marsh apparatus, the glass tube through which the hydrogen was conducted being heated by means of an electric combustion furnace. The deposit of arsenic was carefully weighed on fine analytical balances. By this method very small quantities of arsenic can be accurately determined, as is shown by the reported results.

### THE APPLICATION OF DIPHENYLCARBAZIDE AS INDICATOR IN THE TITRATION OF IRON WITH DICHROMATE.

BY O. L. BARNEBEY AND S. R. WILSON.

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Brandt<sup>1</sup> published, in 1906, a method using diphenylcarbazide,<sup>2</sup> called by him "diphenylcarbohydrazide," as an "inside indicator" for the titration of iron. Shortly after the publication of the article one of us tried the method as outlined by Brandt and by following his directions minutely could not obtain concordant results. A detailed study, however, developed an interesting and valuable modification of this method and likewise an application for the analysis of ores.

In 1900, Cazeneuve<sup>3</sup> pointed out the fact that diphenylcarbazide could be used to detect extremely small quantities of chromic acid, giving the sensitiveness as 1 : 1,000,000. Brandt carries the work further and uses this substance as an indicator for the titration of iron. He states that large amounts of hydrochloric acid and also manganese sulfate solution containing phosphoric acid must be present to prevent too rapid destruction of the indicator. His conditions for titration are 0.2 to 0.7 g. of iron, 60 to 80 cc. dilute hydrochloric acid (sp. gr. 1.12), 100 cc. manganese sulfate solution (containing 6 kg. manganese sulfate, 33 liters dilute sulfuric acid (1 : 3), 3 liters phosphoric acid (sp. gr. 1.7), diluted to 60 liters), diluted to a total volume of 1 $\frac{1}{2}$  liters and 5 cc. of a 0.1% solution of indicator added. Smaller amounts than 0.2 gram of iron may be titrated by slightly modifying the conditions.

The color changes involved are very marked. The first drop of dichromate added gives a pink or red tinge which becomes deep red as the titration proceeds. This color gradually changes to lavender, which seems to be caused by the complementary nature of the red compound and triva-

<sup>1</sup> *Z. anal. Chem.*, 45, 95.

<sup>2</sup> *Beilstein*, Vol. 4, 671.

<sup>3</sup> *Bull. soc. chim.*, 23, 592, 701, 769.