THE ESTIMATION OF MINUTE QUANTITIES OF ARSENIC.

BY H. B. BISHOP.

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THE determination of small amounts of arsenic has been the subject of considerable investigation during the past few years and the test that has received special attention and elaboration is the modified Marsh test. The result has been to perfect this method to such a point that for simplicity and sensitiveness it leaves little to be desired.

Perhaps the most thorough and satisfactory work on this subject that has recently appeared is that of G. Lockemann.[1] His observations upon the necessary precautions and the sensitiveness of the Marsh test have been verified by us and a mirror has been obtained with 1/10,000 mg. arsenic, which is as small an amount as has been detected by him and others.

It is to be noted that the Marsh test is only a part of an arsenic determination and that the preparation of a sample for such a test is often a much more difficult part of the operation. Most substances to be analyzed require a preliminary treatment to obtain the arsenic in a soluble form, free from interfering substances and in a suitable volume. When solution is obtained by a long and tedious oxidation, separation made by a precipitation method or concentration made by evaporation at a high temperature, numerous sources of error arise which necessitate the greatest vigilance to obtain reliable results. The smaller the quantity of arsenic, the greater the difficulty, for it is not only more easily lost but also more easily multiplied by the use of numerous arsenical reagents.

While trying to increase the delicacy of the determination of arsenic in sulphuric acid, a number of experiments were tried to test the accuracy of the evaporation method of concentration. In analyzing sulphuric acid of such purity that a few cubic centimeters do not show any arsenic, it has been customary to take a large sample and evaporate to a small volume suitable for the Marsh apparatus. It was thought that during such a long evaporation small amounts of arsenic might be lost and escape detection. Accordingly, known amounts of arsenic were added to 250 cc. samples of sulphuric acid which previous analysis by evapora-

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[1] Z. angew. Chem., 1905, 416.

ting and applying the Marsh test had shown to be arsenic-free. When 0.000006 per cent. arsenic was added about a half was recovered, and in samples to which 0.000004 per cent. arsenic had been added the arsenic escaped detection, although the sensitiveness of the Marsh test at this time was 0.000001 per cent. arsenic or 0.004 mg. When it was found that these small amounts were volatilized so easily, the method which naturally suggested itself was to distil the arsenic under conditions which would be most favorable for its removal. The well-known method of distilling with ferrous chloride and hydrochloric acid was tried but the result was not satisfactory, as ferrous sulphate was precipitated and produced so much bumping that its use was abandoned. In the method finally adopted, a mixture of hydrochloric and sulphurous acids is forced through a capillary tube into the hot concentrated sulphuric acid. After distilling for one hour while absorbing the escaping gas in water, the distillate containing arsenious chloride, hydrochloric and sulphurous acids is oxidized with potassium chlorate, evaporated on the steam-bath and the Marsh test applied.

SEPARATION OF ARSENIC BY DISTILLATION.

The apparatus shown in Fig. 1 has been devised for carrying out the distillation.

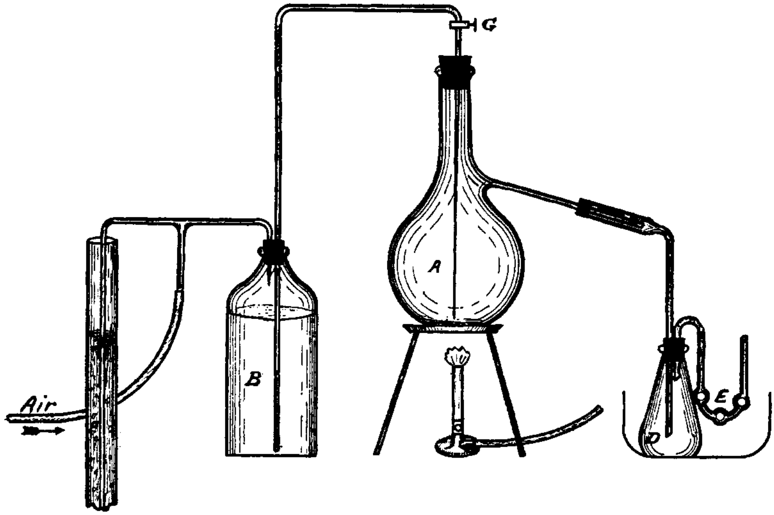

Fig. 1.

The sample is poured into the distilling flask *A* which is connected by a glass tube with the supply bottle *B* containing the sulphurous-hydrochloric acid mixture. The glass tube is provided with a glass stop-cock *C* for regulating the supply of acid and is drawn to a capillary extending to the bottom of *A*. If this tube is not drawn to a capillary, it is liable to break at the surface of the hot sulphuric acid. The side arm of the flask *A* is connected through an adapter with a receiver *D* which has a *U*-tube connection *E* to afford complete absorption of the gas. *D* and *E* are immersed in a basin of cold water. Some pressure is required to force hydrochloric acid through a capillary tube into hot sulphuric acid, and this is obtained by means of compressed air which is connected with *B* and *F* by a **T**-tube and exerts a pressure in *B* proportional to the height of the column of water in *F* (about 3 feet) through which it bubbles. The sample of sulphuric acid (about 95 per cent. H_2SO_4) is heated to 150–200° C. and the supply of the sulphurous-hydrochloric acid mixture regulated so that 50 to 75 cc. are used during a distillation of one hour. The small bubbles of gas formed at the end of the capillary permeate to all parts of the sample, keeping it stirred and in escaping carry the arsenious chloride into the receiver *D* where the gases are absorbed in about 50 cc. of cold water.

The first distillate usually contains all the arsenic, a second sometimes a trace, while a third and even a fourth distillation can be made to prove its complete removal and the absence of arsenic in the apparatus and reagents.

The distillate in *D* and *E* is poured into a casserole, oxidized with a pinch of potassium chlorate and evaporated on the steam-bath to 5–10 cc. and until all free chlorine has been expelled. It is then washed into the Marsh apparatus with a few cubic centimeters of 15 per cent. sulphuric acid.

In constructing the apparatus rubber connections have been avoided, and corks have been used in the bottle and flasks, as small amounts of arsenic have been traced to the use of rubber.

MARSH TEST.

The apparatus shown in Fig. 2 represents the most sensitive form used in this work.

The capacity of *A* is about 10 cc. and is provided with a ground glass stopper which can be removed for charging and cleaning.

The lower end of *A* communicates with a funnel tube *C* having a glass stop-cock. *D* is a side arm tube filled with neutral calcium chloride for drying the gas, and to it is attached a hard glass tube *E*. This is drawn to a capillary and passes through a wire gauze chimney *F* at which point it is heated by a Bunsen burner.

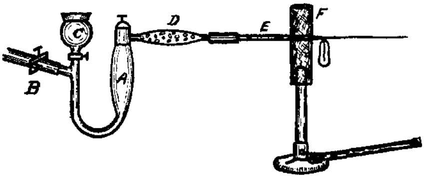

Fig. 2.

To make a test, a few pieces of copper-plated zinc are placed in the tube *A* and the air is removed from the apparatus by a stream of carbon dioxide, obtained from a cylinder, entering at the tube *B* and regulated by a screw pinch-cock. After running for a few minutes it is stopped and the sample introduced through *C*. The arsine is decomposed by passing through the heated tube and the arsenic deposits in the capillary at a point cooled by a wet cotton string wound once around the tube and dipping into a small tube of water. Each test is allowed to run for one hour, observing the same conditions as in preparing the standard mirrors, and by comparing the mirror thus obtained with the standard set, the amount is estimated.

REAGENTS.

Ordinary chemically pure hydrochloric acid contains so much arsenic that it is entirely unfit for use in this work without previous purification. This is done by distillation, keeping it well oxidized by the addition of potassium chlorate. Since authorities differ in their ability to prepare arsenic-free hydrochloric acid in this way, it may be well to describe the apparatus used. It consists of a large supply bottle containing hydrochloric acid oxidized with potassium chlorate which is fed through a siphon into the bottom of a 2-liter distilling flask containing about 500 cc. of concentrated sulphuric acid. The flask is gently heated and the escaping hydrochloric acid carrying some chlorine is scrubbed and dried by bubbling consecutively through two more 2-liter flasks containing about a liter each of cold concentrated sulphuric acid and finally absorbed in a bottle of distilled water immersed in a cooler. By introducing a little chlorine in this way with the hydrochloric acid, the arsenic is kept oxidized, in which form it is not volatile at the temperature used, and any arsenic that might be mechanically carried over is removed by the sulphuric acid scrubbing. The resulting acid 20–22° Bé. is saturated with gas obtained from a cylinder of liquid sulphur dioxide, which removes the free chlorine. The reagent thus formed, if not absolutely arsenic-free, contains less than enough to affect an analysis as proved by blank determination. The same holds for the small amounts of potassium chlorate and sulphuric acid that are used in oxidizing the distillate and in making the Marsh test.

Arsenic-free shot zinc, such as is used in the Marsh test, is usually so pure that it does not react readily with acid, and the most satisfactory method of obtaining zinc that will give a good evolution of gas is to treat it as recommended by Lockemann with a 0.5 per cent. solution of copper sulphate which has been recrystallized. The zinc, black in appearance, is washed with water, dried on a filter-paper and preserved in a closed vessel until wanted for use. The only other reagent used is calcium chloride which as Lockemann also notes should be neutral. The ordinary dry chemically pure calcium chloride on the market is alkaline and when used in this form interferes with the sensitiveness of the test. It is therefore dissolved by heating with a small amount of water and neutralized or made slightly acid with hydrochloric acid, evaporated in a casserole while stirring until it begins to solidify, the stirring being continued while it cools so as to produce small lumps, the neutrality of which is proved by testing with phenolphthalein. It is then put into a closed vessel to preserve it till needed.

The arsenic solution used for preparing the standard mirrors is made by dissolving 1.320 grams of pure arsenious oxide (= 1 gram arsenic) in 25 cc. of sulphuric acid and 10 cc. of nitric acid. When the arsenic has dissolved, water is added and the solution evaporated on the steam-bath to expel the nitric acid. It is then successively diluted and divided until a solution containing the desired amount of arsenic is obtained. For an apparatus of the size described, the largest mirror is made by using an amount of the solution corresponding to 0.01 mg. arsenic and for the smallest 0.0001 mg. arsenic.

EXPERIMENTAL.

ARSENIC IN SULPHURIC ACID.

In order to test the sensitiveness and accuracy of this method, 2-liters of 95 per cent. chemically pure sulphuric acid were freed from arsenic by distilling as described above until the final distillate did not show any arsenic, then 0.004 mg. of arsenic was added and by means of the above method, it was recovered and accurately determined. This is a determination of one part of arsenic in a billion of sulphuric acid or 0.0000001 per cent. arsenic. A sample of special sulphuric acid was subsequently analyzed and duplicate analyses showed it to contain 0.000,00006 per cent. arsenic, which is probably the smallest percentage of any element that has been quantitatively separated and determined.

ARSENIC IN BRIMSTONE.

The determination of arsenic in brimstone has been even more difficult than in sulphuric acid, for it has been thought necessary to completely oxidize the sample before making the determination, and when the sample is a large one, a long treatment with large quantities of reagents is required. It was thought that this difficulty could be avoided by adding the sample of brimstone to purified sulphuric acid and then making the above separation and determination. When sulphur is added to hot concentrated sulphuric acid, it melts and floats through the acid in fine globules which having about the same density as the hot acid, are liable to settle, become superheated and crack the flask. Several flasks were broken in this way before the cause and remedy were found. It was apparent that the density of the acid was not high enough and it was therefore increased by the addition of sodium sulphate. Chemically pure sodium sulphate was tried but it contained so much arsenic that an equivalent amount of sodium hydroxide was substituted. To obtain the desired result 250 cc. of chemically pure sulphuric acid (95 per cent.) are poured into a casserole and 16 grams of chemically pure sodium hydroxide are cautiously added a little at a time. The heat of the reaction evaporates the excess of water so that when the solution has cooled, it is ready to be poured into the distilling flask and freed from arsenic as described above. The sample of brimstone is then added and after heating until a fine emulsion is obtained, the distillation is made and the arsenic estimated by the Marsh test.

A sample of brimstone that had been carefully analyzed by oxidation with bromine and nitric acid, evaporated to expel oxidizing agents and found to contain 0.002 per cent. arsenic, was tested by this method and found to contain 0.010 per cent. arsenic. Another sample of brimstone in which arsenic could not be detected when 25 grams were oxidized with fuming nitric acid, evaporated to expel nitric and tested in the Marsh apparatus, was analyzed by the above method and found to contain 0.00002 per cent. arsenic.

ARSENIC IN ORGANIC MATTER.

Most methods that have thus far been proposed for the determination of arsenic in organic matter have required its preliminary destruction by oxidation, fusion or combustion, and any one who has tried these methods is fully aware of the difficulties encountered.

While determining arsenic in sulphuric acid it seemed possible that organic substances might be added directly to the concentrated sulphuric acid, and have their arsenic removed by distillation without any preliminary treatment other than digestion in the acid to obtain solution of the arsenic.

To test this application of the method, a potato was obtained from a field where the vines had been sprayed with Paris green. The sample was thoroughly washed, dried, ground to a powder and 10 grams gradually added to 250 cc. of sulphuric acid in a distilling flask which a previous distillation and Marsh test had proven to be arsenic-free. After digesting hot for several hours and until the particles seemed thoroughly disintegrated, a distillation with the sulphurous-hydrochloric acid mixture was made, and a Marsh test of the distillate showed 0.01 mg. arsenic or 0.0001 per cent. arsenic. When we consider that on a wet basis this is only 0.00002 per cent., the potato containing about 76 per cent. of water, there is no need to fear arsenic poisoning from this source.

SUMMARY.

The separation of arsenic from concentrated sulphuric acid by distillation with sulphurous and hydrochloric acids and its subsequent estimation by the Marsh test, is a method well adapted for the determination of minute quantities of arsenic in sulphuric acid and, in general, in those substances that are soluble in or decomposed by hot concentrated sulphuric acid. The special advantages are that large samples may be taken, comparatively few reagents are required and interfering substances are not introduced into the Marsh apparatus, so that it can be operated under standard and uniform conditions.

A MODIFIED WESTPHAL BALANCE FOR SOLIDS AND LIQUIDS.

BY F. M. WILLIAMS.

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THE advantages of the Westphal balance as a rapid and accurate means for the determination of the specific gravity of liquids are well recognized.

It occurred to the writer that this instrument might be so modified as to extend its use to the determination of the specific gravity of solids. Attempts have been made to use it with solids by means of heavy solutions, such as Thoulet's and Penfield's by diluting the liquid until the solid immersed will neither sink nor float, and then taking the gravity of the liquid in the ordinary way. But the maximum gravity obtainable by such solutions is about 4.5 and the operation is cumbersome and tedious.

The modifications in the old form may be readily seen from the accompanying drawing. It will be noted that the pointer has been lengthened and upon this at a distance equal to the length to the other arm, a notch has been placed for the reception of a special support carrying two pans, one below the surface of the liquid, and the other above. By this means an object may be weighed in air and then in liquid by interchanging the pans, or by transferring to the lower pan.

For convenience in adjustment a two-piece counterpoising weight is made to move along the threaded portion of the pointer. By having the counterpoising weight in two pieces one part serves as a lock-nut preventing accidental changes of adjustment.

A further modification tending to prevent wear upon the knife edges is a cam device for raising the beam and locking the same securely in place.

The balance has been made much more compact and portable by inserting a hinge joint in the upright standard arm, allowing the instrument to be folded to a space $2^3/_4 \times 2^3/_4 \times 10$ inches.

Owing to the comparatively unsatisfactory methods for the