

official figures of the Board, a bonus of \$402,500 over and above the contract price will be paid to the builders.

CONTRIBUTIONS TO PRACTICAL RAILROAD INFORMATION.

Chemistry Applied to Railroads.

SECOND SERIES.—CHEMICAL METHODS.

IX.—METHOD OF DETERMINING TIN IN PHOSPHOR BRONZE.

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(Continued from page 321.)

OPERATION.

DISSOLVE 1 gram of fine borings in 20 c.c. of C. P. nitric acid, 1.20 specific gravity, and evaporate at a temperature not exceeding 225° F., until the residue will not adhere to a dry glass rod. Add 15 c.c. of concentrated C. P. nitric acid, 1.42 specific gravity, heat where the temperature is about 275° F. for 10 minutes, add 30 c.c. of distilled water, stir thoroughly, allow to settle a little, and then filter, washing with distilled water, until a drop of the filtrate evaporated on a piece of clean platinum foil leaves no residue. Set the filtrate aside to be used later in the determination of the lead and copper. Put the filter with the hydrated metastannic acid on it back into the same beaker, taking care to spread out the filter, and add 150 c.c. of yellow ammonium sulphide. Digest with a cover on the beaker at a temperature of about 212° F. for a couple of hours, with occasional stirring. Nearly all, and in some cases all, the tin dissolves as sulphide, the phosphoric acid goes into solution, while most of the copper, iron, lead, etc., which may be present, remains as sulphides suspended in the liquid. Filter into a beaker holding about 25 fluid ounces, and wash with dilute sulphide of ammonium wash water, and at last with water alone, until the volume of the filtrate and washings amounts to about 250 c.c. Dilute the filtrate and washings with distilled water until the volume is about 400 c.c., and then precipitate the tin sulphide with concentrated C. P. hydrochloric acid, adding it cautiously with stirring, and only adding sufficiently slight excess to react clearly with litmus paper. Cover the beaker and put it where the temperature is about 100° F., and allow to stand one night. Dissolve the sulphides in the filter in dilute nitric acid, and wash thoroughly with water. Add the filtrate to the beaker containing the copper and lead salts. Burn off the filter, ignite at a high temperature in porcelain crucible, weigh and add the weight to the binoxide of tin obtained from the precipitated sulphide. After standing over night, decant the clear liquid above the sulphide of tin through a filter, taking care to get as little as possible of the precipitate on the filter; then add about 150 c.c. of water to the beaker, stir thoroughly, and allow to settle clear. Decant the clear liquid through the same filter, and then add about 150 c.c. of acetate of ammonia water, stir thoroughly, and allow to settle clear and decant as before. Repeat this last operation twice more, provided the second addition of acetate of ammonia wash water settles off clear at once; then pour the precipitate on the filter and wash with the acetate of ammonia wash water until the washings no longer react with nitrate of silver solution. If, after the second addition of acetate of ammonia wash water, the precipitate settles a little slowly, and there is a tendency to a turbid liquid above the precipitate, omit the third addition of acetate of ammonia wash water, and proceed to pour the precipitate on the filter, and finish the washing on the filter as above described. Put the filter and precipitate, still wet, into a porcelain crucible, "smoke off" the filter very slowly, and continue the heating over the burner at low temperature, after the filter has disappeared, until the odor of sulphurous acid is no longer perceptible. Gradually raise the temperature with the burner, finish with an intense heat, and then weigh.

APPARATUS AND REAGENTS.

The apparatus required by this method is simply the ordinary beakers, measuring glasses, etc., common to every laboratory, and requires no special comment.

The nitric acid 1.20 specific gravity is made from the stronger by dilution with water. The dilute nitric acid used to dis-

solve the sulphides on the filter is a mixture of one part concentrated C. P. with four parts of distilled water.

The yellow ammonium sulphide is made by dissolving 1 oz. of precipitated sulphur in a 5-lb. bottle of what is known in the market as ammonium hydrosulphide, or hydrosulphuret.

The ammonium sulphide wash water is made by adding one part by volume of commercial C. P. ammonium hydrosulphide to nine parts by volume of water.

The acetate of ammonium wash water is made by nearly neutralizing concentrated C. P. acetic acid 1.04 specific gravity with concentrated C. P. ammonia 0.90 specific gravity, and then adding one part by volume of this solution to three parts by volume of distilled water.

CALCULATIONS.

Atomic weights used: Tin, 118; oxygen, 16; molecular formula, SnO_2 . Since 78.67 per cent. of the binoxide is metallic tin, the weight found expressed in grams, multiplied by this figure, gives the amount of metallic tin in 1 gram of the bronze. Then the amount in 100 grams, or the per cent., would be found by multiplying this figure by 100. This may be briefly expressed by the rule: Express the weight of binoxide found in grams, move the decimal point two places to the right, and multiply by 0.7867. The product will be the per cent. of tin in the bronze. Thus, if the weight found is 0.1284 gram, the percentage will be $[12.84 \times 0.7867]$ 10.10 per cent.

NOTES AND PRECAUTIONS.

It will be observed that this method oxidizes the tin and separates it from the principal portion of the lead, copper, iron, etc., by nitric acid, finishes the separation as completely as ammonium sulphide will do, and removes the phosphoric acid by dissolving the separated metastannic acid in yellow ammonium sulphide, precipitates the tin as sulphide along with much separated sulphur, and converts this sulphide into binoxide for weighing by careful ignition.

The evaporation to dryness needs to be managed with some care. If the temperature is too high, and especially if the action of the heat at high temperature is too prolonged, there will be difficulty with the subsequent solution in ammonium sulphide. On the other hand, if the evaporation to dryness is not carried far enough, the separated metastannic acid is apt to be slimy and give difficulty in the subsequent filtration. A little experience will enable the right point to be reached without difficulty. The treatment of the separated metastannic acid with hydrochloric acid either with or without the addition of potassium chloride to assist the subsequent solution in ammonium sulphide is not necessary if the evaporation to dryness is properly managed, and this procedure introduces complications in the analysis which are better left out.

Fifteen c.c. of concentrated C. P. nitric acid are added to take up the copper and lead salts, after the evaporation to dryness, because approximately this amount of nitric acid is needed in the solution during the subsequent determinations of the lead and copper by electrolysis.

We have not succeeded by any manipulation in completely separating copper and iron from metastannic acid by means of nitric acid, and do not, therefore, recommend ignition and weighing the precipitate obtained after taking up the copper, lead, etc., in strong nitric acid, dilution and filtration.

The digestion of the separated metastannic acid with yellow ammonium sulphide with many bronzes takes up all the tin, so that there is almost nothing left to weigh after dissolving the other sulphides on the filter and ignition of the filter. On the other hand, with some bronzes there is apparently always a little tin left undissolved by the ammonium sulphide. Repeated experiments on a bronze showing this peculiarity gave practically the same results each time, so that it is hardly safe to neglect to follow the directions on this point. The weight of this undissolved tin is rarely more than a milligram.

It is well known that sulphide of copper is slightly soluble in yellow sulphide of ammonium. The sulphide of tin obtained is, therefore, apt to be contaminated slightly with sulphide of copper, and the final weight may also be slightly high on account of oxide of copper.

It is not advisable to leave any of the ammonium sulphide wash water in the filter when washing the sulphides of copper, lead, iron, etc., since this would introduce a little H_2S into the solution in which the copper and lead are to be subsequently determined, an addition which is not desirable. On the other hand, it is not desirable to try to wash copper sulphide from the first with pure water for fear of oxidation and loss.

The precipitation of the tin sulphide is a moderately delicate operation. There must be a slight excess of hydrochloric acid, or tin will remain in solution. On the other hand, if there is too much hydrochloric acid, there is danger of its dis-

solving some of the tin sulphide. Furthermore, the litmus paper test is apt to be affected by the H_2S set free. The litmus paper should not be put into the solution and allowed to remain during the neutralization, as it becomes completely discolored by so doing. Test with a fresh piece each time. After some experience is gained, the way the solution settles off after the last addition of acid is a very good indication of the right point. If the precipitate separates slowly, and the liquid above is inclined to be turbid, either too much or too little acid may be present. If too little, a drop or two more may be just right. If too much, add a few drops of ammonia to alkaline reaction and start again. It is advisable to always test the filtrate from the tin sulphide by adding a few drops of hydrochloric acid, if it is not already clearly acid to test paper, and passing H_2S for half an hour; then allowing the liquid to stand for a couple of hours at a temperature of 120° to 130° F. If no precipitate separates at the end of this time, the filtrate may be thrown away. If any precipitate shows, allow to stand over night, collect on a filter, wash thoroughly, ignite and weigh, adding the weight to the amount previously found.

Allowing the precipitated sulphide to stand in a warm place over night may be unnecessarily long, but as all the constituents of a phosphor-bronze are usually determined, allowing the tin to stand over night does not usually cause any delay. It seems to be essential to have the H_2S pass off before filtration, since the precipitate is sparingly soluble in solution of sulphuretted hydrogen.

In washing the tin sulphide, it is essential to remove the ammonium chloride completely, or loss of tin will follow during the ignition. By the method of washing recommended, less than 5 per cent. of the total amount of ammonium chloride present remains with the precipitate when it is put on the filter.

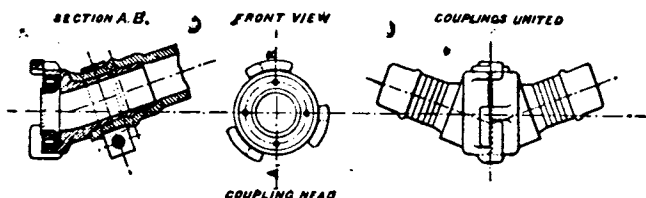


Fig. 1.

It is very difficult to wash tin sulphide mixed with separated sulphur with pure water, on account of the tendency to form a turbid filtrate. As is well known, a slightly acid solution of acetate of ammonia prevents this difficulty. It is advisable, at the very last, to use a much weaker solution of ammonium acetate, so as not to leave too much of this salt with the tin sulphide for fear of reducing some of the tin oxide during the ignition.

The ignition of the wet tin sulphide must be managed with a good deal of caution or there will be either loss of tin sulphide, free sulphur, or sulphuric acid left behind, or some of the oxide of tin reduced. It is believed all these difficulties can be obviated if the ignition is done slowly enough with free access of air. The filter is gotten rid of by "smoking off," which consists in applying the heat to the wet material in the crucible so slowly that the volatile matter of the filter passes off without ignition, free access of air being maintained at the same time. To accomplish this, fold up the wet filter with the tin sulphide in it and place it in the crucible. Put the crucible on the triangle as in ordinary ignitions, and leave the cover off. Then heat the open end of the crucible slowly. The filter and precipitate gradually dry, and soon the parts of the filter in contact with the crucible begin to distill off the volatile matter at low heat, even before the whole is dry. This process goes on if the flame is properly adjusted, until in a little while everything that is volatile at a low temperature has passed away, and the precipitate with a black envelope of carbonaceous matter is left. When this is the case, the temperature can be raised very slowly, the lamp moved back toward the bottom of the crucible a little, and the carbon burned off completely. Many times, when the temperature is raised, the black envelope of carbonaceous matter falls away from the precipitate and is rapidly consumed. The slow heating and free access of air must be continued until the sulphur is all gone. If the heating is done slowly enough, the precipitate is porous, the sulphur apparently all passes away as SO_2 , and there is little danger of volatilizing tin sulphide or reducing the oxide.

In bronzes containing perceptible amounts of antimony the tin cannot be successfully determined by the method given above.

TRAIN HEATING WITH STEAM AND COMPRESSED AIR ON THE EASTERN RAILWAY OF FRANCE.

By M. LANCRENON.

Up to a very recent date the Eastern Railway Company, like the other French companies, has used hot water for heating its trains. Recognizing that this system is frequently insufficient and sometimes even troublesome for passengers, especially on night trains with a long run, we have considered for a long time that its simplicity and the ease with which it can be employed in almost all kinds of cars compensated to a great extent for its disadvantages, at least in our climate, and that there was no need for looking for anything else. But this position could not be indefinitely maintained.

As the movement of passengers and the number of trains increase the reheating and manipulation of the cans become more and more difficult, especially at Paris and in the numerous stations from which local trains start. On the other hand, we were compelled, by the necessities of the operating department, to put cars in service that had a communication from end to end, some of which were intended for trains having a long run, others for short-run trains where fares and tickets could be collected *en route*, as well as the double deck cars in the suburban traffic around Paris. The use of the hot-water cans became almost impossible in these different cars, so that it was necessary to get something else.

The long experience which we have had with thermosiphons did not encourage us to develop that system; the German systems were not applicable to our trains, which must be rapidly and frequently made up and broken. Furthermore, they did not keep the feet of the passengers warm—which, in France, is considered to be very necessary. With these conditions in view, we have been led to examine and experiment with a system which is made the subject of this communication.

Principle of the System.—In studying the operation of the German heating apparatus, I have been struck with the difficulty and the slowness with which the heat reaches the end of the train in general working, with a pressure high enough to ensure the efficient penetration of the steam into the heating pipes. In seeking to determine the cause of this phenomena, it occurred to me that it would be possible to obtain a more even pressure in the pipes by adding a fluid—such as air, for example—to the steam, and one which was not susceptible of being condensed. The first experiment was with a crude apparatus set up in the Villette shops, which confirmed the accuracy of my opinion to such an extent that more complete tests were made with an apparatus which was also set up in the shops, and represented a train of 24 cars of four compartments each. The actual cars were intercalated at different points of the circuit. The arrangements which were developed from this examination after several adjustments were then applied to special testing trains, and finally to trains in service. The principal effect of the air which was added to the steam appears to be the sweeping along and continual carriage of the water of the condensation, which tends to accumulate at low points in the pipes, and which might settle at the discharge openings. We have thus avoided losses due to the accumulation of water and the dangers of freezing. The gaseous current, rendered the more intense by the addition of air, by its friction on the liquid molecules causes them to slide along the walls of the pipes. We know that we can thus cause a liquid to pass through a considerable difference in level by using a pressure far less than the height to be raised; and it is upon this principle that the American steam loop is based, which causes, by means of a simple combination of pipes, the water of condensation produced in a pipe fed by a boiler to be carried back to the boiler. This phenomenon can be shown to a certain extent by causing a liquid to move over any surface whatever by simply blowing above it.

Thanks to the addition of the air, the examination of the best methods to be adopted for heating apparatus was singularly simplified and facilitated. It was possible to obtain a discharge of the water of condensation at each car without fear of freezing at the opening; at the same time we thus did away with an obstacle to the introduction of steam into the heating pipes, and reduced the water of condensation to a minimum, as well as compelling it to follow the general conduit to its end. It was thus possible to use heating pipes in these cars that were very much smaller and of a greater variety of forms, without limiting ourselves to maintaining the inclination which would be necessary to the flow of water that depended on gravity alone. It was also possible, in order to facilitate the regulating, to multiply the pipes, and at the same time control