

THE JOURNAL  
OF THE  
AMERICAN CHEMICAL SOCIETY.

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A NEW METHOD FOR THE DETERMINATION OF ZINC.

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Received October 22, 1898.

PRACTICALLY two methods only are in general use for the gravimetric determination of zinc. Of these, the carbonate method with its many imperfections is being displaced by the phosphate method, at least in this country.

With care the latter will yield excellent results. In our practice it is customary to use ammonium phosphate in place of the usual sodium salt,<sup>1</sup> and after the precipitation of the phosphate to destroy the slight excess of ammonia remaining after heating on the water-bath, by the cautious addition of dilute acetic acid. Under these conditions the filtrate is free from zinc.

Directly igniting the sulphide and filter, and weighing as oxide or sulphide, has been used, but is open to serious objection if the amount of zinc is at all large.

As far as we are aware no one has proposed the solution of the sulphide in nitric acid, the evaporation of the solution so obtained and the conversion of the residue to oxide by ignition. As a second precipitation and washing is avoided it is quicker than the carbonate or phosphate methods and is preferable to

<sup>1</sup> Garrigues : This Journal, 19, 934.

the latter in that the impurities almost invariably present in the zinc precipitate may be easily determined and allowed for.

The sample of ore for analysis (one-half to one gram according to its zinc content) is dissolved and the metals precipitated by hydrogen sulphide separated by the usual methods. After expelling hydrogen sulphide, the solution is colored by bromine water, and the iron and any manganese present are separated by ammonia. The precipitate is dissolved in hydrochloric acid and the precipitation is repeated a second or third time if necessary.

If the ore is one which is known to be free from lime and magnesia the combined filtrates may be boiled down immediately with the addition of an excess of nitric acid to destroy chlorides and ammonium salts. After the removal of the chlorine, the solution is transferred to a weighed platinum dish, evaporated to dryness, ignited and weighed as oxide.

The troublesome filtration and washing of the zinc sulphide should be avoided if possible. In our opinion better results are obtained by the ferrocyanide titration of the solution of the unwashed sulphide than by any gravimetric method involving the filtration and *washing* of this precipitate<sup>1</sup>.

The zinc is best precipitated as follows: Acidulate the warm ammoniacal filtrate from the iron with hydrochloric acid, add a few drops of sulphurous acid to neutralize the bromine set free, then three or four drops of methyl orange.<sup>2</sup> Neutralize with ammonia carefully and add ammonium sulphide drop by drop with constant stirring until a drop of the solution gives a dark coloration with a drop of dilute ferric chloride solution on a porcelain plate, showing a slight excess only of ammonium sulphide. The liquid is now warmed on the water-bath until the sulphide has settled and is filtered through a double ribbed filter. Under these conditions a clear filtrate is invariably obtained, but if washing is attempted the filtrate is frequently cloudy.

<sup>1</sup> C. F. McKenna has suggested to the author that the addition of a little paper pulp to the solution prior to filtration will insure a clear filtrate. If some asbestos is stirred into a cloudy zinc filtrate and the solution passed again through the paper the filtrate will generally be clear. But in any case the slow washing of the precipitate exposes us to a loss through oxidation.

<sup>2</sup> The methyl orange used in exactly neutralizing the solution prior to the ferrocyanide titration and which slightly interferes with the delicacy of the end-reaction, may be readily destroyed after the acidulation by pouring into the beaker a little bromine vapor and stirring this in.

We therefore dissolve directly, without washing, in hot nitric acid (1 : 3) or in dilute hydrochloric acid if cobalt or nickel are present, and correct the weight of the oxide subsequently found for the small amounts of lime or magnesia present. It is well to make a qualitative test for these elements in the filtrate from the sulphide. If absent or in small amount the correction in the weight of the oxide may be omitted.

The solution is boiled down rapidly in a casserole with the addition of nitric acid to expel chlorides. When almost dry the contents are rinsed into a weighed platinum dish or crucible. The evaporation is continued on the water-bath or hot plate until dry, when the nitrate is ignited at the full heat of the Bunsen burner. As some zinc sulphate, which is always present, is not decomposed at this temperature, it is necessary to break up this compound by intense ignition over the blast-lamp. Any lumps should be first broken up by a blunt glass rod. Ammonium carbonate may be used but is liable to occasion some loss.

It may be possible, by igniting at a low heat, to weigh the zinc as sulphate, after evaporating with sulphuric acid. We are working on this now.

After weighing, the oxide is dissolved in hydrochloric acid and the small amount of iron always present thrown down with ammonia, ignited, brushed into the tared watch-glass in the balance and weighed directly. The filtrate is acidulated with hydrochloric acid, heated to boiling, and tested for sulphates with barium chloride. A slight precipitate will usually form but this may, in general, be neglected if the ignition has been properly performed. If in weighable amount it may be treated as in the case of the iron, calculated to sulphur trioxide, and together with the ferric oxide deducted from the weight of the impure oxide.

If lime or magnesia were present the filtrate from the iron should be divided into equal parts, one of which is tested for sulphates and the other for lime and magnesia by throwing out the zinc as sulphide, and testing the filtrate by the ordinary methods. As a rule this is unnecessary unless the lime or magnesia is present in large amounts, for the sulphide is precipitated in dilute solution and the amount of lime remaining in the unwashed sulphide would usually be very small.

The correction for impurities may seem tedious but in reality

it is quickly carried out. Richards has found that zinc oxide obtained by the ignition of the nitrate contains a little occluded nitrogen. This would only amount to a few tenths of a milligram and may be neglected unless unusually accurate work is called for.

For the determination of zinc in alloys containing copper, tin, lead, iron, and zinc, dissolve in nitric acid, evaporate to dryness, and take up with nitric acid if tin be present. Filter and separate copper and lead simultaneously by electrolysis. The solution should contain five to ten cc. concentrated nitric acid in 150 to 200 cc. water. After removing and washing the electrodes carrying copper and lead the solution is evaporated to dryness in a weighed platinum dish and the residue ignited and weighed. Dissolve in hydrochloric acid and separate the usually small amount of iron present by ammonia. Ignite, weigh, and deduct from the weight of the zinc oxide. If nickel be present the weight of the combined oxides may be taken and the nickel afterwards determined, when the zinc may be found by difference.

Zinc in pure spelters is best determined by difference. In impure samples it is sometimes more convenient and equally accurate to determine zinc directly. Dissolve one-half gram in nitric acid and separate the lead electrolytically in a solution carrying ten per cent. nitric acid. Use the platinum cylinder in this case to collect the lead peroxide. Evaporate the solution to dryness in a weighed dish, ignite, and weigh. Dissolve in a little hydrochloric acid, reduce with two to three grams granulated zinc, add sulphuric acid to complete the reaction, dilute with ice water to one liter, and titrate with permanganate. Correct for the amount of iron found. If cadmium, arsenic, or other impurities were present in more than traces the above method would be inapplicable unless modified to include treatment by hydrogen sulphide.

We have not found time to make an extended series of tests of this method but, in numerous analyses of ores and the complete analysis of alloys in which in duplicate analyses the zinc was determined by the well-known methods, the author has convinced himself of the accuracy of the method.