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# DETERMINATION OF SMALL AMOUNTS OF ZINC IN STEELS AND IRONS

By H. A. Bright

ABSTRACT

A comparison of three procedures for the determination of small amounts of zinc in steels and cast irons was made.

The first procedure, which involved the removal of iron by ammonium hydroxide, was found to be rapid and sufficiently accurate for the usual commercial determinations of zinc over a range of 0.005 to 0.30 percent. The second procedure, in which iron is removed by extraction with ethyl ether, was found to be the most satisfactory for amounts of zinc of the order of 0.001 percent. The third procedure, in which the zinc is precipitated by hydrogen sulphide in the presence of iron, gave satisfactory results with 0.003 percent, or more, of zinc in 15-g samples.

The results of analysis of four representative materials showed that the zinc content of steels and irons is very small, of the order of >0.0005 percent.

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## I. INTRODUCTION

As metallurgical science advances, attention is being directed more and more to the effects of small amounts of impurities on the properties of metals. Determination of these impurities, which often occur in very minute amounts, constitutes a special field of analysis, because ordinary methods fail. Although zinc has sometimes been mentioned as a possible constituent of steels and irons,[1] a review of the literature shows but little information on methods for its determination in these materials.

The chief difficulty in any method for the determination of zinc in steel lies in the separation of the minute amount of zinc from the

[1] C. E. Williams and J. D. Sullivan state that zinc, if present in open-hearth steel, exists in very small amounts, probably less than 0.001 percent; cf. "Residual Metals in Open-Hearth Steel", Metals and Alloys, vol. 3, p. 240, 1932, and vol. 4, p. 151, 1933.

large amount of iron. In Ibbotson's method for determining zinc in iron ores,[2] zinc is precipitated as the sulphide from a sulphate solution in which the proper acidity has been obtained by adding ammonium formate and formic acid. In a few tests of this method made by the author satisfactory separations were not obtained in solutions containing 0.5 mg of zinc and 5 to 10 g of iron, probably because of failure to obtain the correct pH for precipitating zinc sulphide. Lundell, Hoffman, and Bright [3] suggest that extraction of ferric chloride by ethyl ether may possibly yield the best results in separating small amounts of zinc from large amounts of iron. Hills [4] recommends precipitation by hydrogen sulphide in a hydrochloric acid solution adjusted to the optimum pH by the addition of sodium citrate and citric acid. In a method for testing ferric chloride for zinc (maximum limit 0.01 percent of zinc), the Committee on Reagents of the American Chemical Society [5] recommends that zinc and copper be separated from the iron by pouring a neutral, or slightly acid, solution of ferric chloride slowly into a relatively large amount of ammonium hydroxide. The mercury cathode, so often a useful tool in analytical chemistry, is not applicable in this problem because zinc, as well as iron, is deposited in the mercury. Neither is the mercuric sulphocyanate method of Lundell and Bee [6] suitable, because precipitation of zinc is always incomplete in the presence of large amounts of iron.

It appeared advantageous, therefore, to investigate the three applicable methods of separation, namely—ammonium hydroxide, extraction with ether, and hydrogen sulphide—as to their suitability for use in the determination of such amounts of zinc as may occur in steel, and, if possible, to develop complete procedures for the determination of this element in steels and irons. It was also planned to make a survey of the zinc content of the Bureau's standard samples of steel and iron. This was abandoned when analyses of four representative samples indicated that if normal steels and irons contain any zinc, the amount must be very small—of the order of $<0.0005$ percent.[7]

## II. EXPERIMENTAL PROCEDURE

Of the separations that have been outlined, three—precipitation by ammonium hydroxide, extraction with ethyl ether, and precipitation by hydrogen sulphide—were tested on solutions of certain steels by themselves and with added amounts of zinc. All of these separations leave zinc with certain other elements, such as copper and molybdenum, which must be removed before the final precipitation of zinc. These elements are removed best by precipitating with hydrogen sulphide in solutions of moderate acidity (2.5 percent). Zinc can then be determined in the filtrate by precipitation as the sulphide in 0.01 *N* acidity [8] followed by ignition of the filtered sulphide to oxide.

[2] F. Ibbotson, The Chemical Analysis of Steel Works' Materials, p. 229. Longmans Green & Co., London, 1920.

[3] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, "Chemical Analysis of Iron and Steel", p. 387, John Wiley & Sons, New York, 1931.

[4] F. G. Hills, Anal. Ed. Ind. Eng. Chem., vol. 5, p. 201, 1933.

[5] Anal. Ed. Ind. Eng. Chem., vol. 4, p. 154, 1932.

[6] G. E. F. Lundell and N. K. Bee, Trans. Am. Inst. Metals, vol. 8, p. 146, 1914.

[7] The complete, or nearly complete, absence of zinc can probably be attributed to the relatively low boiling point of zinc (906 C), a temperature considerably below the melting point of iron or steel, and to the ease with which it is oxidized in the furnace or cupola.

[8] The best precipitation of zinc sulphide is obtained in a sulphuric acid-sulphate solution, cf. "Applied Inorganic Analysis." Hillebrand and Lundell p. 331, John Wiley & Sons, New York, 1929.

Descriptions of the procedures for the three methods investigated are given in the following sections, II 1, 2, and 3. In all cases blanks were carried through all operations and deducted before calculation of the amount of zinc found.

Obviously zinc-free glassware, pyrex for example, must be used if determinations of minute amounts of zinc are in question. Furthermore, the use of a rubber policeman is to be avoided unless it is known to be free from zinc.

## 1. PRECIPITATION WITH AMMONIUM HYDROXIDE

In the ammonium hydroxide method the sample is dissolved in sulphuric acid, the solution poured slowly into a considerable excess of ammonium hydroxide, and filtered. The filtrate is boiled to remove most of the ammonium hydroxide, made slightly acid (about 2.5 percent by volume) with sulphuric acid, and treated with hydrogen sulphide to precipitate members of the hydrogen sulphide group, such as copper and molybdenum. The solution is again filtered, the filtrate boiled to remove hydrogen sulphide, and the acidity adjusted to 0.01 *N*. The zinc is then precipitated as the sulphide which is ignited to the oxide.

### (a) PROCEDURE

Transfer 5 g (if the zinc content exceeds 0.05 percent use 1 to 2 g) of the sample to a 400-ml pyrex beaker, add 30 ml of diluted sulphuric acid (1+3)[9] and 75 ml of water. Cover, and heat gently, with occasional shaking, until reaction ceases. (With cast irons, or high molybdenum steels, filter at this stage through a rapid paper and wash several times with warm water.) Cool slightly and add 50 ml of a freshly made 20 percent solution of ammonium persulphate (not less than 85 percent purity). Boil the solution about 8 minutes. If manganese dioxide is precipitated add sulphurous acid, drop by drop, until the solution clears.

Boil for about 2 minutes, dilute to 200 ml and pour the warm solution (70 to 80 C) slowly and while stirring into 95 ml of diluted ammonium hydroxide (25 ml water + 70 ml of ammonium hydroxide + 4 g of ammonium sulphate)[10] contained in a 400-ml beaker. Let settle for a few minutes and filter, by suction, through a large rapid paper, or Büchner funnel, and wash once with a diluted solution of ammonium hydroxide (1+25, containing 2 g of ammonium sulphate per liter). If the zinc content exceeds 0.03 percent the precipitate should obviously be washed several times.

Boil the filtrate until the volume has been reduced to about 150 ml. Add 2 drops of methyl orange (0.1 percent), treat with diluted sulphuric acid (1+1) until the color changes to red and then add 7.5 ml. of the acid in excess. Pass hydrogen sulphide through the solution for about an hour, let settle for 15 to 20 minutes and filter through a tight paper. (With molybdenum steels, the solution shoud be heated to about 75 C and maintained at that temperature during the passage of hydrogen sulphide.) Wash the precipitate a few times with a diluted solution of sulphuric acid (1+99) containing hydrogen sulphide.

Boil the filtrate until hydrogen sulphide has been expelled (10 to 15 minutes) and cool to 20 C. (With molybdenum steels a small

[9] The symbol (1+3) indicates here, and throughout this paper, one volume of the concentrated acid sp gr 1.84 diluted with three volumes of water.

[10] Ammonium sulphate is not as necessary with small as with large amounts of zinc, but is added because it involves no great trouble or expense and will take care of the exceptional case, cf. E.G.R. Ardagh, Ind. Eng. Chem., vol. 16, p. 298, 1924, who uses a similar solution for washing ferric hydroxide precipitates free from zinc.

precipitate may result at this stage and should be removed by filtration.) Add two drops of methyl orange solution, and then ammonium hydroxide (filtered) until the solution just turns yellow. Add *N* sulphuric acid until the yellow color changes to orange and then add 1.0 ml for each 100 ml of solution. The volume of solution at this point should be about 150 to 175 ml and the strength of the acid and the amount added must be carefully watched in order that the solution shall not be more acid than 0.01 *N*. Cool to room temperature, and pass a rapid current of hydrogen sulphide through the solution for 60 minutes. Let stand for at least 3 hours and filter through a small tight paper, containing a little paper pulp. Wash 10 to 12 times with cold water. Char the paper and precipitate at a low temperature in a small weighed porcelain crucible, burn the carbon at as low a temperature as possible (without flaming) and then gradually raise the temperature to 900–950 C.[11] Cool in a desiccator and weigh. Subtract the blank obtained for the whole series of operations, and calculate the percentage of zinc.[12] The results obtained by this method are given in table 1.

TABLE 1—*Determination of zinc in steels and irons*

[Separation of iron by precipitation with ammonium hydroxide]

| Material and weight of sample used | Zn added | ZnO obtained | Percentage of zinc | | Error |
|---|---|---|---|---|---|
| | | | Added | Found | |
| | *mg* | *mg* | | | *Percent* |
| 5 g of steel 8d [1] | 0.25 | 0.2 | 0.005 | 0.003 | −0.002 |
| 5 g of steel 8d | .25 | .3 | .005 | .005 | .000 |
| 5 g of iron 107 | .3 | .3 | .006 | .005 | −.001 |
| 5 g of steel 8d | .5 | .7 | .01 | .011 | +.001 |
| 5 g of steel 65a | .5 | .6 | .01 | .010 | .000 |
| 5 g of iron 107 | .5 | [2] .6 | .01 | .010 | .000 |
| 5 g of iron 107 | .5 | .5 | .01 | .008 | −.002 |
| 5 g of steel 8d | 3.0 | 3.2 | .06 | .051 | −.009 |
| 1 g of steel 8d | 2.0 | 2.5 | .20 | .20 | .00 |
| 1 g of steel 8d | 3.0 | 3.7 | .30 | .29 | −.01 |

[1] Compositions: no. 8d, bessemer steel, C=0.078, Mn=0.482, Si=0.018, Cu=0.013, Ni=0.004, Cr=0.007, V=0.003, Mo=0.003, Sn=0.002, As=0.007; no. 65a, acid electric steel, C=0.258, Mn=0.748, Si=0.441, Cu=0.176, Ni=0.242, Cr=0.178, V=0.006, Mo=0.005, Sn=0.024, As=0.012; no. 107, nickel-chromium-molybdenum cast iron, C=2.57, Si=2.34, Cu=0.074, Ni,=0.807, Cr=0.455, V=0.015, Mo=0.687, As=0.01.
[2] Ignited oxide dissolved in diluted sulphuric acid, both sulphide precipitations again made, and the zinc sulphide again ignited to the oxide.

## 2. EXTRACTION WITH ETHYL ETHER

In the ether method most of the iron is separated from the zinc by treating a hydrochloric acid solution of the sample with ethyl ether.[13] The extracted acid solution is then treated with sulphuric and nitric acids, evaporated to fumes of sulphuric acid, diluted, and poured into ammonium hydroxide. From this point the procedure is the same as described for the ammonium hydroxide method, II, 1 (a).

[11] Zinc oxide is very slightly volatile at 1,000 C. Zinc will be volatilized and lost as metal at lower temperatures if carbon still remains. If the ignited oxide is not of normal appearance (yellow when hot and white when cold), it must be dissolved in diluted sulphuric acid and both precipitations with hydrogen sulphide repeated.

[12] If the net weight of the ignited precipitate is less than 0.2 mg, the amount of zinc is best estimated nephelometrically by the ferrocyanide method as follows: Dissolve the ignited oxide in 20 ml of diluted hydrochloric acid (1+9) and transfer to a Nessler tube. Add 0.1 g of potassium chloride and dilute to exactly 50 ml. Add exactly 1 ml of a freshly prepared 2 percent solution of potassium ferrocyanide. Shake and compare in a few minutes with a series of suitable standards (e.g., 0.05, 0.10, 0.20 mg of zinc) prepared at the same time and in exactly the same manner. To obtain good results by the nephelometric method it is essential that unknown and standards be treated exactly alike. For further details see "The Nephelometric Analysis of Zinc." L. T. Fairhall and J. R. Richardson. Jour. Am. Chem. Soc., vol. 52, p. 938, 1930.

[13] $ZnCl_2$ is reported by F. Mylius and C. Hüttner, Ber., vol. 44, p. 1315, 1911, as being slightly extracted (0.2 percent) by ether. With the small amounts of zinc involved in this investigation, this factor is negligible.

### (a) PROCEDURE

Transfer 25 g of sample to an 800-ml pyrex beaker and add 200 ml of diluted hydrochloric acid (3+1). Cover and heat gently, with occasional shaking until reaction ceases. (With cast irons cool, dilute to 250 ml, allow carbonaceous matter to settle, filter through a rapid paper and wash several times with water.) Oxidize the ferrous iron by slowly adding about 30 ml of diluted nitric acid (1+1) and gradually heating to boiling. The oxidizing action is apt to be quite rapid, in which case it should be checked by momentarily immersing the beaker in cold water. Boil or evaporate the solution until the volume has been reduced to about 50 ml, add 30 ml of hydrochloric acid and again evaporate to a volume of about 50 ml. Add 250 ml of diluted hydrochloric acid (sp gr 1.11) and cool the solution to room temperature. Transfer to a liter separatory funnel, cool the container and contents to 5 C and add 550 ml of cp ethyl ether.[14] Carefully shake the funnel for a few minutes and then allow the two layers to separate for about 10 minutes. Draw off the lower (acid) layer into the original 800-ml beaker. Warm the extracted acid portion on a steam bath until free from excess ether and then boil down to a volume of about 50 ml. Add 14 ml of diluted sulphuric acid (1+1) and 15 ml of nitric acid (spgr 1.42) cover, and boil for a few minutes. Remove the cover glass, evaporate to fumes of sulphuric acid, and continue the fuming for a few minutes.

Cool, add 100 ml of water, heat until salts are dissolved and pour the warm solution (70 to 80 C) into 100 ml of diluted ammonium hydroxide (1+1), containing 5 g of ammonium sulphate. Filter, wash the precipitate, and treat the filtrate as in method II, 1 (a). The results obtained by this method are given in table 2.

TABLE 2.—*Determination of zinc in steels and irons*

[Separation of iron by extraction with ether]

| Material and weight of sample used | Zn added | ZnO obtained | Percentage of zinc | |
|---|---|---|---|---|
| | | | Added | Found |
| | *mg* | *mg* | | |
| 50 g of steel 8d [1] | | 0.1 | | [2] <0.0001 |
| 25 g of steel 65a [3] | | 0 | | |
| 25 g of steel 65a | | 0 | | |
| 25 g of steel 22b [3] [4] | | 0 | | |
| 50 g of iron 107 [1] | | 0.1 | | [2] .0001 |
| 50 g of steel 8d [1] | 0.50 | 0.4 | 0.0010 | .0006 |
| 25 g of steel 8d | .50 | .5 | .0020 | .0016 |
| 25 g of steel 65a | .50 | [5] .6 | .0020 | .0019 |
| 25 g of iron 107 | .50 | [5] .7 | .0020 | .0022 |
| 25 g of steel 8d | 2.50 | 2.6 | .0100 | .0083 |

[1] Ether extracted solutions of two 25-g samples combined.
[2] Estimated nephelometrically.
[3] Spectroscopic examination of this steel by W. F. Meggers, Bureau of Standards, showed no evidences of the presence of zinc.
[4] No. 22b, Bessemer steel, C=0.674, Mn=0.935, Si=0.123, Cu=0.009, Ni=0.003, Cr=0.003, V=0.005, Mo=0.002, Sn=0.004, As=0.004.
[5] Ignited oxide dissolved in diluted sulphuric acid, both sulphide precipitations again made, and the zinc sulphide again ignited to the oxide.

[14] The ether supplied in tin cans was found to contain detectable amounts of zinc, probably originating from the soldering flux used in fabricating the containers. In the work described herein anhydrous ether, analytical reagent quality, was used.

### 3. PRECIPITATION WITH HYDROGEN SULPHIDE

In this method the sample is dissolved in diluted sulphuric acid (1 + 5) and filtered. The acidity of the solution is adjusted to about pH 2.5 by the use of a citric acid-sodium citrate solution,[15] and zinc together with other precipitable sulphides is precipitated by hydrogen sulphide. The precipitated sulphides are filtered, washed, and then digested with diluted sulphuric acid (1 + 9) After filtration, any members of the hydrogen sulphide group still remaining in the solution are removed, and then zinc is precipitated as sulphide as in II, 1 (a).

#### (a) PROCEDURE

Transfer 15 g of sample to a 500-ml pyrex erlenmeyer flask and add exactly 96 ml (6 ml for each gram of sample plus 6 ml in excess) of diluted sulphuric acid (1 + 5) Cover with a watch glass and heat gently. When action ceases, filter through an 11-cm rapid paper into a 600-ml pyrex beaker, and wash several times with warm water.

Dilute the filtrate to 450 ml, add 5 g of ammonium sulphate, 60 ml of citrate solution (20 g of citric acid and 450 g of sodium citrate dissolved in water, filtered, and diluted to one liter) and stir well.[16] Pass a current of hydrogen sulphide through the solution for 1 hour. Let stand for about 4 hours, or preferably overnight under a bell jar.

Filter through an 11 cm tight paper, containing some paper pulp, and wash a few times with cold water. Return the paper and contents to the original beaker, add 55 ml of diluted sulphuric acid (1 + 9) and boil gently to expel hydrogen sulphide (10 to 15 minutes). Filter through a 9-cm rapid paper and wash with warm water. Add a few drops of methyl orange solution to the filtrate and neutralize with ammonium hydroxide. Then add sufficient diluted sulphuric acid (1 + 1) to make the solution about 2.5 percent acid. Treat with hydrogen sulphide, filter through a tight 9-cm paper, and precipitate zinc in the filtrate, etc., as directed in section II, 1 (a). The results obtained by this method are given in table 3.

TABLE 3.—*Determination of zinc in steels and irons*

[Separation of zinc by precipitation with hydrogen sulphide]

| Material and weight of sample used | Zn added | ZnO obtained | Percentage of zinc | |
|---|---|---|---|---|
| | | | Added | Found |
| | *mg* | *mg* | | |
| 15 g of steel 8d | 0.40 | [1] 0.4 | 0.0027 | 0.0021 |
| 15 g of steel 8d | .40 | [1] 0.4 | .0027 | .0021 |
| 15 g of steel 8d | 1.00 | [1] 1.2 | .0067 | .0064 |
| 15 g of steel 65a | 1.00 | [1] 1.1 | .0067 | .0059 |
| 15 g of iron 107 | 1.00 | 1.1 | .0067 | .0059 |
| 5 g of steel 65a | 5.0 | 6.4 | .10 | .102 |
| 15 g of steel 22b | 15.0 | 19.1 | .10 | .102 |

[1] Ignited oxide dissolved in diluted sulphuric acid, both sulphide precipitations again made, and the zinc sulphide again ignited to the oxide.

[15] The Nephelometric Analysis of Zinc. L. T. Fairhall and J. R. Richardson. Jour. Am. Chem. Soc. vol. 52, p. 938, 1930. The Determination of Zinc in Biological Materials, W. R. Tood and C. H. Elvehjem, Jour. Biol. Chem., vol. 96, p. 609, 1932. F. G. Hills, cf. footnote 4, p. 384.

[16] The pH of the solution at this point should be about 2.5 and can, if desired, be checked as follows: Pour about 15 ml of the solution into a small beaker and add two drops of thymol blue indicator (0.04 percent). The solution should be yellow. If red, more citrate must be added. The acidity of the solution is determined in a small portion because the color of the large volume of iron solution is too deep. The test portions are subsequently added to the main solution.

## III. SUMMARY

Summarizing the data given in tables 1, 2, and 3, together with observations made during the work, it can be said that, (1) the ammonium hydroxide method is fairly rapid and surprisingly accurate for separating zinc from iron in 5–g samples containing from 0.005 to 0.06 percent of zinc. This procedure should also yield good determinations of zinc in 1–g samples of zinc-bearing iron ores; (2) extraction by ethyl ether appears to be the most suitable method for removing large amounts of iron from very small amounts of zinc, and (3) the hydrogen sulphide method yields satisfactory results with 15–g samples containing 0.003 percent, or more of zinc. A limited number of experiments with this method involving more iron and less zinc were not entirely satisfactory, probably because the proper acidity for the initial sulphide precipitation was not obtained.

The results of analysis of four representative materials showed that the zinc content of steels and irons is very small, of the order of $<0.0005$ percent.

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