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QUALITATIVE MICROANALYSIS OF NON-FERROUS METALS

GEORGE W. BROWN AND LOTHROP SMITH

During summer vacations, part of my school expense was earned as a purchaser of non-ferrous scrap metal for a small Chicago smelter. In such purchasing, it is very necessary to know something of the general composition of the metal. For example, in buying soldered articles, it is of vital importance to know whether the solder is high in tin or lead, and whether it contains antimony or bismuth. Other purchasers to whom I have talked have reported the same difficulty.

It is common practice in the purchase of metal from large smelters, to take the vendor's word for the composition, as the only alternatives are either an expensive analysis by a commercial laboratory, or the establishment of a laboratory by the small foundry. Such a laboratory is ordinarily of limited use, and the expense is too high for practical justification.

An example of such a problem is one encountered by the firm of Christensen and Olsen of Chicago, who contracted to make small cast gears out of an alloy called 85-5-5-5, which is composed of Cu, Sn, Pb and Zn. The initial orders of castings proved satisfactory, but a subsequent large order was rejected because it was found that lead had accumulated in small globules throughout the castings making them very difficult to machine. The large smelter which furnished the metal for that order disclaimed responsibility, but analysis by a commercial laboratory showed the presence of a small amount of aluminum in the alloy, which would have the effect of causing the lead to segregate. The cost of the delay and rejection to the small foundry was several hundred dollars, and a series of such incidents could easily endanger profitable operation.

Such trouble can be avoided by qualitative analysis, provided that the expense of equipment and upkeep is not prohibitive. With this end in view, an attempt was made to apply the methods of qualitative microanalysis to some of the problems involved in the purchase of scrap.

Limiting the applications to non-ferrous alloys simplified the procedure in that fusions are not involved, and that a uniform

method of solution with aqua regia could be specified. Such simplifications are of particular advantage where it is necessary to employ an analyst with a rather low level of technical training.

APPARATUS AND REAGENTS

Only twelve pieces of apparatus are needed for an analysis of the average metal sample. These are listed in Table I. The centrifuge is the only piece costing over \$1.50. For extreme portability, the centrifuge may be eliminated, but it was found to be a great convenience and is preferably included.

Fifty-one reagents are needed, and while some are fairly expensive, large amounts are not necessary, and one set of reagents should last for a considerable time. These reagents are shown in Table II.

Tests were selected for 22 elements commonly found in non-ferrous alloys. Each test was tried upon one or more alloys containing the element to be identified, and the most conclusive test adopted for inclusion in the outlined procedure. One of the critical points lies in the avoidance of contamination, and it is therefore recommended that stock bottles be used as the main source of reagent. The small portions of reagent used for each determination may then be discarded to avoid possibility of contamination.

TABLE I
LIST OF APPARATUS

Spot plate	Eye droppers
Centrifuge	Small vials for reagents
Centrifuge cones	Black spot plate
Micro pipets	Micro porcelain crucible
Gutzeit apparatus	Micro burner or alcohol lamp
Heavy filter paper	Casserole

TABLE II
LIST OF REAGENTS

1. Acetic acid (2N)
2. Alkali stannate reagent (Dissolve 5 g. of stannous chloride in 5 cc. of concentrated HCl. Dilute with water to 100 cc. When ready to use, mix with an equal volume of 25% (8N) NaOH solution.)
3. Alpha-nitroso-beta-naphthol (Dissolve 2 g. of alpha-nitroso-beta-naphthol in 100 cc. of glacial acetic acid and dilute with 100 cc. of water.)
4. Alizarin (0.01% solution, 0.6N in acetic acid and 3N in sodium acetate.) (Make up fresh)
5. Aluminon reagent (0.1 g. of aurin tricarboxylic acid is mixed with 50

- cc. of water and enough concentrated ammonia added to make 100 cc. of solution.)
6. Ammonia (Concentrated)
 7. Ammonium carbonate (5N)
 8. Ammonium chloride (Saturated solution)
 9. Ammonium molybdate (Add 35 cc. of nitric acid (Sp. gr. 1.2) to 100 cc. of a 5% solution of ammonium molybdate.)
 10. Ammonium mercuric thiocyanate (9 g. of ammonium thiocyanate and 8 g. of mercuric chloride are dissolved in 100 cc. of water.)
 11. Ammonium phosphate (5N)
 12. Ammonium sulphide (Concentrated) (Make up fresh by bubbling hydrogen sulphide through concentrated ammonia.)
 13. Antipyrine (Solid)
 14. Antipyrine-thiocyanate reagent (Add solid antipyrine to 2N potassium thiocyanate reagent.)
 15. Benzidine (Dissolve 0.05 g. of benzidine in 10 cc. of glacial acetic acid. Dilute to 100 cc. with water.)
 16. Bromine water
 17. Cuprous chloride solution
 18. Dimethylglyoxime (1% alcoholic solution)
 19. Diphenyl-carbazide (1% alcoholic solution) (Make up fresh)
 20. Diphenyl-carbazide thiocyanate (To a saturated solution (alcoholic) of diphenyl carbazide, add potassium thiocyanate crystals to saturation.)
 21. Dithizon (Diphenyl thiocarbazone) (0.002% in carbon tetrachloride.)
 22. Hydrochloric acid (Concentrated) (6N) (0.1N)
 23. Hydrogen peroxide (3%)
 24. Iodine in 1N KI solution
 25. Lead chloride (Saturated solution)
 26. Magnesium metal (Powdered)
 27. Nitric acid (Concentrated) (6N)
 28. Oxalic acid (2N)
 29. Para-dimethyl-amino-benzal rhodanine (0.03% in acetone)
 30. Phenol (Solid)
 31. Phosphomolybdic acid (5%)
 32. Phosphoric acid (Concentrated)
 33. Potassium chromate (1N)
 34. Potassium cyanide (5% solution)
 35. Potassium hydroxide (1N)
 36. Potassium iodide (1N)
 37. Potassium thiocyanate (Solid) (2N solution)
 38. Quinalizarin (Dilute solution in 0.1N NaOH)
 39. Silver nitrate (Solid)
 40. Sodium acetate (Solid) (Saturated solution)
 41. Sodium carbonate (Saturated solution)
 42. Sodium hydroxide (8N) (6N) (2N) (0.1N)
 43. Sodium phosphate (2N)
 44. Sodium tartrate (Saturated solution)
 45. Sodium thiosulphate (Solid) (1N solution)
 46. Stannous chloride (Solid) (1N solution in concentrated HCl)

47. Sulphuric acid (Concentrated) (6N)
48. Tartaric acid (Solid) (Concentrated solution)
49. Thiourea (10% solution)
50. Zinc metal (Powdered)
51. Zinc sulphate (2N)

PROCEDURES

In all cases the metal to be analyzed is treated in a centrifuge cone with aqua regia. If there is a residue, filter and treat the precipitate with concentrated HCl. (Test the HCl soluble portion for Al.) If a residue still remains, filter and treat the precipitate with concentrated ammonia water. A black or grey precipitate indicates the presence of Hg, but the test for Hg should be carried out also. To the filtrate, add dilute nitric acid. A white precipitate indicates the presence of silver.

Aluminum

Add one drop of the aluminon reagent to three drops of the unknown solution. Add an excess of ammonium carbonate solution. If a pink color persists, Al is present. A blank should be run for comparison. Be interferes with this procedure, and if present, the following alternate procedure should be used.

To two drops of the acid unknown, add ammonia until just alkaline plus one drop in excess. Add 3 drops of alizarin solution. A red or pink coloration indicates the presence of Al.

Antimony

Two drops of the aqua regia solution are heated to boiling on a watch glass and a few crystals of sodium thiosulphate are added. If Sb is present, there is a brown or red precipitate. With a blank there is a yellow precipitate.

Arsenic

Place a small piece of the unknown metal in the gutzeit apparatus, add a few grains of Zn and a little dilute sulphuric acid. Place a loose plug of cotton saturated with cuprous chloride in the body of the tube, and a piece of filter paper with a crystal of silver nitrate on it over the mouth of the apparatus. A brown coloration of the crystal indicates the presence of As. A blank should be run for comparison.

Beryllium

Make two drops of the solution to be tested alkaline with 6N NaOH, then slightly acid with dilute HCl. To one drop of this solution on the spot plate, add one drop of 0.1N NaOH. Then test with one drop of quinalizarin. If Be is present there is a light blue color. A blank gives a purple color.

Chromium

Mix one drop of the unknown solution with one drop of bromine water on the spot plate. Add one drop of 6N NaOH and a crystal of phenol. Then add a drop of diphenyl-carbazide and a drop of concentrated sulphuric acid. There is a deep violet coloration in the presence of Cr. Mo and V interference can be inhibited with oxalic acid.

Bismuth

Place one drop of the aqua regia solution on a spot plate, add one drop of lead chloride solution, 1 drop of 2N NaOH and 1 drop of KCN solution. Add two drops of alkali stannate reagent, and mix by stirring. A distinct brown color will be obtained within three minutes if Bi is present.

Cadmium

Mix on the spot plate 1 drop of freshly prepared diphenyl-carbazide thiocyanate with one drop of solution and 1 drop of ammonia. A violet coloration indicates the presence of Cd. Co interferes.

Cobalt

Take, in a watch glass or centrifuge cone, 1 drop of solution, 1 drop of ammonium chloride, 2 drops of ammonia, and 2 drops of water. Filter. To 2 drops of the filtrate, add 2 drops of phosphoric acid, 1 drop of potassium iodide and 2 drops of sodium thiosulphate. Filter. To 2 drops of this filtrate add one drop of alpha-nitroso-beta-naphthol and one drop of HCl. A brown coloration indicates the presence of Co. The last portion of this test should be carried out on a spot plate.

Copper

Make solution alkaline with 6N NaOH, then just acid with dilute nitric acid. Add one drop of the acid solution to one drop of

ammonium phosphate, 1 drop of zinc sulphate, and 1 drop of ammonium mercuric thiocyanate in a casserole and warm. A positive test is indicated by a violet color. Co and Ni interfere.

Gold

Mix one drop of solution, 1 drop of stannous chloride, and one drop of KCNS, and boil in water. A purple color indicates the presence of Au. Hg interferes.

Iron

One drop of solution, 1 drop of KCNS, and 1 drop of 0.1N HCl are mixed on a spot plate. A deep brown on red precipitate indicates the presence of Fe.

Lead

One drop of solution, 3 drops of potassium cyanide, 1 drop of ammonium chloride, and one drop of dithizon are mixed on a spot plate. A pink coloration indicates lead. A blank should be run for comparison. (The reagent should be a deep green color and should not be over two months old.)

Magnesium

One drop of solution and 2 drops of KOH are mixed on the spot plate. Add enough of a solution of iodine in 1N KI to color the spot a dark brown. Then add KOH until the solution is yellow in color. If a dark brown precipitate persists, it is an indication of Mg. A blank should be run for comparison.

Manganese

A drop of the test solution is treated on filter paper with NaOH, then a drop of tartaric acid solution is placed in the middle of the moist spot, followed by benzidine. A blue color indicates Mn.

Mercury

One drop of solution and four drops of sodium phosphate are mixed in a centrifuge cone. Filter. One drop of the filtrate and one drop of a saturated solution of Para-dimethyl-amino-benzal rhodanine in alcohol are mixed on the spot plate and solid sodium acetate added. A red color appears in the presence of Hg.

Molybdenum

Make slightly alkaline with NaOH and filter off any precipitate which forms. Put one drop of concentrated HCl, one drop of KCNS, one drop of stannous chloride and one drop of the unknown on the spot plate. A deepening of the red color indicates the presence of Mo. A blank should be run for comparison.

Nickel

Use a spot plate. Mix 1 drop of solution with 1 drop of 3% hydrogen peroxide, 1 drop of saturated sodium tartrate solution, 2 drops of saturated sodium carbonate solution and one drop of alcoholic dimethylglyoxime. A red precipitate indicates the presence of Ni. A red coloration alone is not an indication of Ni.

Phosphorus

Make the solution slightly alkaline with NaOH, then slightly acid with dilute HCl. Use one drop of this solution on the spot plate with 2 drops of ammonium molybdate, 1 drop of benzidine and 3-6 drops of sodium acetate. Stir well after the addition of sodium acetate. A blue color indicates the presence of P.

Silver

Make solution alkaline with NaOH, then acid with dilute HCl. Take 2 drops of this solution with 2 drops of ammonium carbonate and centrifuge. On the spot plate take two drops of the filtrate; add one drop of potassium chromate and one drop of acetic acid. Let stand for one minute. A red coloration or precipitate indicates the presence of Ag.

Tin

Take three drops of the aqua regia solution on a spot plate and add a few grains of solid tartaric acid. Then add ammonia until the solution is alkaline. Take one drop of this solution on the spot plate and add one drop of freshly prepared ammonium sulphide reagent. Absorb the excess liquid; add one drop of HCl and a few grains of powdered Mg. Take one drop of this solution, and add one drop of phosphomolybdic acid. A blue color indicates the presence of Sn. The above test for Sn is specific even in the presence of Sb.

Vanadium

Two drops of the aqua regia solution are mixed with one drop of concentrated sulphuric acid and one drop of hydrogen peroxide on a spot plate. A pale pink to brown color indicates that V is present. A blank should be run for comparison.

Zinc

Place a drop of the solution on a watch glass, and heat with NaOH. Filter. Acidify the filtrate with acetic acid. Filter if a precipitate forms and treat three drops of the filtrate on a black spot plate with 2-5 drops of anti-pyryne-thiocyanate reagent. A white precipitate indicates the presence of Zn.

In many cases I found that the micro procedures were definitely superior to the type of procedure usually followed and being limited to non-ferrous alloys, many short cuts could be used. An example is the test for tin. Usually, if antimony is present in the same alloy as tin there is trouble and interference. The usual method of testing an alloy of this sort is to evaporate with nitric acid, treat the residue with sodium hydroxide to make alkaline and then add potassium sulphide solution. This is then heated on a water bath for some time and diluted and acidified with hydrochloric acid to precipitate the tin and antimony as sulphides. Next the precipitate is freed from sulfur. Then the tin and antimony sulphides are heated with concentrated hydrochloric acid, diluted, heated and saturated with hydrogen sulphide. The precipitate is then finally tested for antimony and the solution for tin, if through this involved procedure you haven't forgotten what you were looking for. As a contrast to this procedure, I found the following micro procedure for tin which works even in the presence of antimony. The metal is put into solution in aqua regia on the spot plate, treated with tartaric acid and then ammonia until alkaline. One drop of this solution and one drop of ammonium sulphide are mixed, one drop of hydrochloric acid and a few grains of magnesium are added. This solution then gives a blue color with phosphomolybdic acid if tin is present.

CONCLUSIONS

I believe that qualitative microanalysis is the answer to the problem for the small industrialist. The reagents and complete set of equipment take up very little space and may be stored in a corner to be used only as the need arises. Also it is not necessary

to have advanced training in chemistry to be able to carry out the tests. It is simply a matter of following directions and watching for the proper colors. An afternoon of practice is probably all that is needed for a man to become a relatively skilled operator with microtechniques. In addition the procedure is rapid and inexpensive. The man in industry is always in a hurry and speed and economy are vital. In the example given of the Chicago foundry, the managers would have gladly given fifty dollars to solve their problem and also satisfy the customer immediately. For this amount of money they could have a complete set of micro-equipment and could solve not only that problem, but many similar to it.

The field buyer of metal could also carry equipment enough with him to analyze samples of goods that he intended to buy. Thus transactions would be speeded up and the buyer would feel free to offer what the metal was worth without discounting for the possibility of being cheated.

In short, I feel that micro-procedures in this limited field are definitely an asset and should be brought to the attention of the industrialist.

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