

EXPERIMENTS ON THE ANALYSIS OF PIG COPPER, BRASSES, AND BRONZES.

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IN a recent number of this JOURNAL (January, 1894) a preliminary note was given on a method for systematic examination of pig copper and high copper percentage alloys. It is proposed in this paper to present some of the experiments involved in the work of which the note was a résumé. The results are familiar to those working in copper analysis, but on taking up the subject I was not able to find in the literature accessible to me quantitative data of many current statements. It is known, for instance, that in determining tin in copper alloys by solution in nitric acid that phosphorus and arsenic remain in their oxidized forms with the metastannic acid but it was sought to ascertain whether the reaction was quantitatively exact or whether phosphorus and arsenic were still to be looked for in the filtrate from the residue.

Taking up tin the question was as to how that metal alloyed with copper reacted during analysis. The usual method of determining tin in such alloys is by solution in nitric acid, evaporating off excess of acid, diluting and when the precipitate has settled, filtering. The points to be taken into consideration are:

1. Whether or not the metastannic acid formed is soluble in nitric acid. Experiment answers this negatively.
2. Whether or not the metastannic acid is soluble in ammonium hydroxide, ammonium nitrate, or both. Experiment answers this also negatively.
3. The state of purity in which the residue is obtained. It is a matter of experience that in nitric acid solution, especially when evaporated to a point where basic salts are liable to form, the stannic oxide is found to be more or less contaminated with such salts of copper, manganese, and iron. These impurities adhere most tenaciously and washing with dilute nitric acid will not remove them completely. The reaction of tin phosphate and arseniate holds quite rigidly. The attack on tin by nitric acid is a solution and conversion into

an oxidized form and in this reaction if phosphoric or arsenic acids be present the stannic phosphate or arseniate is formed which, like the bismuth salts, is insoluble in nitric acid of five per cent. or less strength. The importance of this reaction in copper analysis is very great. With the exception of certain special alloys the tin present will generally exceed the quantity necessary to hold the arsenic and phosphorus in an insoluble form and the phosphate and arseniate of tin are not readily decomposed by simple digestion with alkali sulphide (S_n) but require fusion.

The following experimental results were obtained. Expressed in grams or fractions thereof. The term "metastannic acid" is used to indicate the residue obtained on dissolving tin in nitric acid, but such residue also contains stannic acid.

I. Solubility of the metastannic acid or residue obtained on dissolving pure tin in nitric acid. Excess of acid removed by evaporation to pasty condition. Dilution forty cc. Filtered after twelve hours.

Tin taken.....	1368	1544	1610	1744	1623	1674
Tin found.....	1365	1557	1620	1745	1630	1683

II. Solubility of the metastannic acid or residue obtained. Dissolving the tin in excess of nitric acid. Present 6.92 free nitric acid. Dilution 150 cc. Filtered after twelve hours.

Tin taken.....	1812	1734	1795	1808	1746
Tin found.....	1812	1738	1792	1800	1732

III. Solubility of the metastannic acid or residue obtained. Dissolving in nitric acid. Evaporating to paste. Diluting to forty cc. and digesting twelve hours with five grams ammonium nitrate.

Tin taken.....	1963	1822	1763	0600	1814	1280
Tin found.....	1965	1842	1784	0602	1839	1301

IV. Solubility of the metastannic acid or residue obtained. Conditions as in III. Digesting twelve hours with 6.52 NH_3 .

Tin taken.....	1653	1472	1785	1530	1671	1242
Tin found.....	1679	1498	1808	1563	1690	1260

V. Solubility of metastannic acid or residue obtained. Conditions as in III and IV. Digesting twelve hours with five grams $NH_4NO_3 + 6.52 NH_3$.

Tin taken.....	1495	1527	1357	1731	1567	1511
Tin found.....	1534	1567	1408	1784	1606	1546

VI. Precipitation of tin by NH_4HO . Five grams of copper present 6.92 free HNO_3 . Ammonia added at once to re-resolution of the copper salt. Filtered after twelve hours. All contaminated with copper oxide. Washed with dilute nitric acid.

Tin taken.....	1986	1770	1779	1928	1977
Tin found.....	2095	1907	1866	1998	1958

VII. P_2O_5 remaining with metastannic acid. Excess of tin present. Phosphor-tin treated with nitric acid. Evaporated to paste. Dilution forty cc. Present 0.0631 phosphorus in one gram.

Phosphor-tin taken.....	3150	2580	2763	2400	0990
P in filtrate	0003	trace	trace	0004	trace
Per cent. P in residue ...	99.905	99.983

VIII. P_2O_5 remaining with metastannic acid. Excess of phosphorus present. Conditions as in VII. Present 0.0250 phosphorus.

Tin present.....	0078	0076	0067	0077	0075
P combined.....	0190	0146	0131	0151	0154

The ratio of SnO_2 : P_2O_5 is 1: 4 (on averaging).

IX. As_2O_5 remaining with metastannic acid. Excess of tin present. The arsenic and tin treated with nitric acid. Conditions as in VII. Present 0.0067 arsenic.

Arsenic in filtrate	0012	0009	0011	0012	0011
Per cent. As in residue ...	83.5	86.6	83.6	83.6	83.6

X. As_2O_5 remaining with metastannic acid. Excess of arsenic present. Conditions as in IX. Present 0.0134 arsenic. In filtrate.

Arsenic.....	0129	0121	0129	0107	0113
Per cent. loss	3.73	11.19	3.73	20.15	15.67

In both IX and X tin and arsenic were attacked by nitric acid in presence of each other. In IX there was a large excess of tin (0.1000 gram). In X there was 0.0095-0.0110 tin present. The operations were conducted in the same manner and repeated.

XI. Phosphate of tin with metastannic acid. Digested at 70° for five hours with excess Na_2S .

Phosphorus present.....	0071	0046	0069	0061	0136
P as unconv'd phosphate ..	0024	0018	0041	0037	0114
Per cent. unconverted.....	33.8	37.1	59.4	60.3	83.8

No 5. (83.8) in solution in nitric acid was inadvertently carried to complete dryness.

XII. Arseniate of tin with metastannic acid. Digested at 70° for five hours with ammonium sulphide. Filtered from residue after twelve hours. Present 0.0067 arsenic.

As as unconv'd arseniate ..	0051	0057	0055	0058	0057
Per cent. unconverted.....	76.12	85.07	82.09	86.56	85.07

The residue, acids of tin, were converted by ignition in a porcelain crucible, to stannic oxide. The full heat of a Fletcher lamp was used. Phosphorus was precipitated by molybdic solution and weighed as $Mg_2P_4O_{11}$. Arsenic was weighed as $Mg_2As_2O_7$.

With antimony a number of similar experiments were carried out. The antimony was weighed as Sb_2O_3 and Sb_2S_3 .

XIII. Solubility of the residue obtained by dissolving pure antimony in dilute nitric acid (1-3) evaporated to pastiness. Dilution forty cc. Filtered after twelve hours.

Antimony taken	1004	1186	1198	1243	1120
Antimony found	0947	1151	1170	1232	1017

XIV. Residue as in XIII. Nitric acid solution containing 6.92 free nitric acid. Dilution 150 cc. Filtered after twelve hours.

Antimony taken	2214	2166	2244	2600	2277
Antimony found	2046	1829	2079	2537	2160

XV. Residue as in XIII. Digested twelve hours with 6.52 NH_3 . Dilution forty cc.

Antimony taken	1012	1000	1584	1278	1100
Antimony found	0982	0965	1551	1272	1038

XVI. P_2O_5 remaining with the oxides of antimony on solution of metallic antimony in nitric acid. Excess of antimony present. Evaporated to pastiness. Dilution forty cc. Present 0.0051 phosphorus.

Phosphorus in filtrate....	0020	0033	0018	0018	0015
Per cent. P in residue ...	60.78	35.29	64.70	64.70	70.59

Antimony is a most troublesome determination to make in copper analysis. If it can be separated and obtained in a precipitate of small bulk the solubility of the sulphide in alkali sulphide can be taken advantage of, but to apply this reaction in

the presence of ten to twenty grams of copper in the form of an easily oxidized sulphide is a difficult and tedious operation.

The object of the use of ammonia and barium hydrate is to effect for copper what is done in iron analysis for single determinations. In separating manganese or phosphorus in a steel one of the objects is to retain the iron in solution, precipitating out the element which is present only in small quantity. The bulk of the copper being held in solution by the ammonia and precipitation being completed by barium hydrate the analysis of a pig copper is simplified by having a small precipitate to work upon. An excess of barium hydrate being used the separation of the crystalline barium carbonate probably has its effect in the filtration. If we have to make a systematic examination of a copper alloy, as in any case the residual tin oxide obtained by the nitric acid method would have to be purified, it is easier to do this work of purification and separation in such a way as to obtain quantitative results of the different minor constituents sought. If there is enough iron, tin, etc., to fix all the phosphorus and arsenic in an insoluble form the results are quantitative for these elements. To add ferric chloride to obtain such results may be of advantage, but iron is an important object of search in such examination and these two elements are not difficult to separate from the main bulk of copper by other methods. Only special alloys, such as phosphor-bronze or a manganese-copper alloy made with ferro-manganese contain notable quantities of phosphorus. Phosphorus is also sometimes present in aluminum brass, and a sample was found to contain 0.056 per cent. P to 0.22 Fe. Where phosphorus and arsenic are used as deoxidizers, only a very small quantity is to be found on analysis.

To properly precipitate iron, aluminum, or bismuth by ammonia it is necessary to avoid a large excess of the reagent, but in adding ammonia to re-solution of the copper salt an excess must be added and retained. Using test solutions for examination of the use of ammonia and barium hydrate the following results from sixty odd experiments were obtained:

Element.	NH_4HO .	$\text{NH}_4\text{HO} + \text{Ba}(\text{HO})_2$.	Dilution.
Phosphorus.....	not precipitated.	{ not precipitated completely.	100 cc.
Arsenic.....	"	precipitated.	50 cc.
Nickel.....	"	not precipitated	"
Cobalt.....	"	"	"
Zinc.....	"	"	"
Cadmium.....	"	"	"
Silver.....	"	"	"
Bismuth.....	ppt. incomplete.	ppt. complete.	150 cc.
Manganese.....	"	"	"
Antimony.....	"	{ coloration by H_2S , trace in solution.	"
Tin.....	ppt. complete.	ppt. complete.	"
Lead.....	"	"	"
Iron.....	" (?)	"	"

With arsenic in the ammoniacal solution of fifty cc. dilution the precipitation by $\text{Ba}(\text{HO})_2$ is complete, as barium ammonium arseniate (Douglass and Prescott, Qual. Anal.). In dilute solutions or on heating the precipitation becomes incomplete. Digestion with alkali sulphide (S_{11}) does not transpose this precipitate. Phosphorus is precipitated as barium phosphate. With a copper containing known quantities of the minor constituents the following results by the use of ammonia and barium hydrate were obtained: The original copper taken contained 0.03 per cent. Fe and 0.025 per cent. Pb as impurities. Allowance was made in calculating.

Element.	Present.	Taken	Taken	Taken	Taken	Taken
		10	20	30	40	50
		grams	grams	grams	grams	grams
		Cu	Cu	Cu	Cu	Cu
Arsenic.....	0079	0053	0051	0081	0079	0073
Tin.....	0041	0048	0043	0043	0030	0040
Antimony....	0048	0051	0050	0042	0045
Lead.....	0053	0052	0056	0056	0060	0057
Bismuth.....	0028	0030	0030	0026	0029	0034
Cadmium.....	0295	0309	0307	0291	0221
Phosphorus...	0032	0024	0037	0029	0021
Dilution in cc.		300	400	(800)	800	800

The difficulty arising in the use of thirty, forty, or fifty grams of the pig copper came from the separation of the copper-ammonium salts. The dilution was 800 cc. It also takes the equivalent quantity of potassium cyanide to decolorize the filtrate. If

the solution is allowed to stand but thirty to sixty minutes the copper salt is much diminished in quantity and the precipitate appears to be all down. Ten grams and a dilution of 150 cc. works well. The copper-ammonium salts are readily soluble in water on warming, and if arsenic and phosphorus are in the form of iron or other insoluble salt they are not affected by such treatment. The above results were obtained: By dissolving in nitric acid, adding ammonium hydroxide to re-solution of the copper salt followed by addition of excess of barium hydroxide, such excess being quickly indicated by the formation of the crystalline barium carbonate. Allowed to stand 30 to 120 minutes and filtered. Filtrate decolorized by potassium cyanide and precipitated by hydrogen sulphide.

In the July (1893) number of this JOURNAL Mr. Jesse Jones applies a method for the determination of manganese in bronzes based on Ford's method in steel analysis. In the course of the method as described he removes copper by hydrogen sulphide, filters and obtains the manganese from the filtrate. His paper simply describes the course of analysis without entering into any details as to why it was found necessary to remove the copper. In making some analyses for Mr. F. Lynwood Garrison (*Jour. Frank. Inst.*, June to September, 1891), Hannay's reaction, the oxidation and precipitation of manganese as manganese dioxide in the nitric acid solution by potassium chlorate, was applied at once and without removing copper. It was the suggestion of the late Dr. F. A. Genth to try this method as conducted in the analysis of steel and subsequent examination of the filtrate gave negative results for manganese. I have repeated the experiments to find out whether or not removing copper is a source of error and the results given below were obtained on a manganese brass, dissolved in nitric acid and made up to 100 cc. Aliquot portions were then taken, the manganese precipitated by potassium chlorate and titrated in neutral solution by permanganate. The variation is within reasonable limit and shows, I think, that there is no objection to proceeding with a copper alloy in the manner as with steel and that the removal of copper is not essential to accuracy.

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I wish to acknowledge the kindness of Prof. F. A. Genth to whose encouragement was largely due the idea of putting these data into form, and of Mr. F. Lynwood Garrison to whom I am indebted for a number of alloys from his collection.

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INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

SUB-COMMITTEE ON METHODS.

BULLETIN No. 1.

ORGANIZATION AND WORK OF THE COMMITTEE.

AT the World's Congress of Chemists, in Chicago, last August, following the papers of Professor J. W. Langley, "On the Work of the Committee on International Standards for the Analysis of Iron and Steel," and of Dr. C. B. Dudley, "On the Need of Standard Methods for the Analysis of Iron and Steel, with Some Proposed Standard Methods," was a brief discussion, which resulted in the reference by that body of the whole subject of standard methods for the analysis of iron and steel, to the Committee on International Standards for the Analysis of Iron and Steel. That committee, it will be remembered, consists of seven chemists, in each of five different countries, namely, England, France, Germany, Sweden, and the United States. The American Committee was appointed jointly by the American Society of Civil Engineers, and the University of Michigan, with Professor J. W. Langley, Case School of Science, Cleveland, Ohio as Chairman. The other members of that Committee were W. P. Barba, Midvale Steel Works, Nicetown, Philadelphia, Pa., A. A. Blair, 406 Locust street, Philadelphia, Pa., Professor Regis Chauvenet, President State School of Mines, Golden, Colorado, Professor T. M. Drown, Mass. Inst. Technology, Boston, Mass., Dr. C. B. Dudley, Chemist Penn'a. R. R. Co., Altoona, Pa., and Porter W. Shimer, Easton, Pa.

Following the reference of the subject to this committee, it