

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 52

CAST BRONZE

| Analyst | Copper | Tin | Zinc | Lead as PbSO ₄ | Lead as PbO ₂ | Antimony | Nickel | Iron |
|--------------|--------|------|------|---------------------------|--------------------------|----------|--------|------|
| 1..... | 88.36 | 7.88 | 1.88 | 1.52 | 1.53 | 0.14 | 0.12 | 0.12 |
| 2..... | 88.32 | 7.80 | 1.91 | 1.55 | 1.56 | .18 | .14 | .11 |
| 3..... | 88.33 | 7.94 | 1.93 | | 1.52 | .19 | .13 | .10 |
| 4..... | 88.35 | 7.92 | 1.94 | | 1.49 | .15 | .14 | .12 |
| 5..... | 88.32 | 7.89 | 1.90 | | 1.58 | .12 | .16 | .14 |
| 6..... | 88.37 | 7.87 | 1.82 | 1.48 ^a | 1.52 | .16 | .12 | .12 |
| 7..... | 88.29 | 7.87 | 1.86 | | 1.54 | .16 | .12 | .13 |
| 8..... | 88.34 | 7.87 | 1.87 | 1.50 | | .15 | .13 | .13 |
| 9..... | 88.30 | 7.90 | 1.86 | | 1.55 | .14 | .11 | .14 |
| 10..... | 88.35 | 7.91 | 1.88 | 1.50 | 1.54 | .17 | .12 | .08 |
| 11..... | 88.41 | 7.83 | 1.87 | 1.51 ^a | | .13 | .14 | .10 |
| 12..... | 88.35 | 7.94 | 1.90 | | 1.51 | .18 | .14 | .10 |
| 13..... | 88.26 | 7.92 | 1.86 | | 1.54 | .16 | .12 | .11 |
| 14..... | 88.34 | 7.95 | 1.93 | { 1.52 ^b | | .14 | .13 | .15 |
| | | | | { 1.53 | | | | |
| 15..... | 88.32 | 7.99 | 1.89 | | 1.49 | .14 | .14 | |
| Average..... | 88.33 | 7.90 | 1.89 | 1.52 | 1.53 | .16 | .13 | .12 |
| | | | | 1.52 | | | | |

^a Lead as chromate.

^b Lead as molybdate.

INDEX TO ANALYSTS

- J. A. Scherrer, Bureau of Standards.
- The American Brass Co., Waterbury, Conn.
- The Bridgeport Brass Co., Bridgeport, Conn.
- Wm. B. Price and F. M. Barry, Scovill Manufacturing Co., Waterbury, Conn.
- The Ajax Metal Co., Philadelphia, Pa.
- W. A. Cowan and W. J. Brown, National Lead Co., Brooklyn, N. Y.
- B. Woyski and H. McKay, Lumen Bearing Co., Buffalo, N. Y.
- G. K. Elliott and S. A. Weigand, The Lunkenheimer Co., Cincinnati, Ohio.

- A. B. Beaver, The National Cash Register Co., Dayton, Ohio.
- H. W. Maack and S. Wilner, Crane Co., Chicago, Ill.
- A. M. Smoot and A. Craig, Le Doux & Co., New York, N. Y.
- H. C. Parrish, A. D. Little, Inc., Cambridge, Mass.
- Dr. F. N. Pease, Pennsylvania R. R. Co., Altoona, Pa.
- J. E. Virchow and O. W. Staib, C., B. & Q. R. R. Co., Aurora, Ill.
- J. Strauss, Naval Gun Factory, Washington, D. C.

S. W. STRATTON,
Director.

Washington, D. C.

11-7742

July 6, 1921.

OUTLINES OF THE METHODS USED IN THE ANALYSIS OF THE BUREAU OF STANDARDS LEAD-BASE BEARING METAL STANDARD SAMPLE No. 53.

METHOD EMPLOYED AT THE BUREAU OF STANDARDS

One portion of the alloy was dissolved in aqua regia, oxides of nitrogen were driven off, and the solution was diluted and warmed to get lead chloride in solution. The solution was then made alkaline with potassium hydroxide, treated with hydrogen sulphide, digested, and filtered. The sulphides of lead, bismuth, copper, and iron were dissolved in aqua regia and again treated as above. The purified sulphides were dissolved in aqua regia and the solution was treated with sulphuric acid and heated till fumes of sulphuric acid escaped. The solution was cooled, diluted, and the lead sulphate filtered off, washed, and ignited in the usual manner. The sulphuric acid filtrate from the lead was diluted, treated with hydrogen sulphide, and filtered. The filtrate was used for the determination of iron as oxide corrected for silica, while the sulphides were dissolved in nitric acid and the bismuth was thrown out as the oxychloride. The oxychloride was dissolved in nitric acid and the bismuth was precipitated as the basic carbonate, which was filtered off, dissolved in nitric acid, and the evaporated solution ignited to Bi_2O_3 in a tared platinum crucible. The filtrate from the bismuth oxychloride precipitation was treated with hydrogen sulphide; the sulphides were dissolved in nitric acid and electrolyzed for copper and residual lead.

Separate 2-gram samples were dissolved in 20 cc of sulphuric acid, made up to 250 cc volume, treated with 20 cc of hydrochloric acid, brought to boiling, cooled to 10°C and titrated with a standard solution of permanganate, with deduction of the calculated effect of arsenic. The titrated solution was then treated with 80 cc of hydrochloric acid, reduced with test lead under carbon dioxide, cooled to 10°C , and titrated in the presence of carbon dioxide with iodine.

Arsenic was distilled from a separate portion, precipitated as silver arsenate, and the washed precipitate dissolved and titrated by Volhard's method.

METHODS EMPLOYED BY THE COOPERATING ANALYSTS

(2) *Determination of iron, copper, and bismuth.*—The sample was dissolved in aqua regia and lead separated as lead chloride by cooling and the addition of alcohol. The filtrate from the lead chloride separation was boiled, oxidized with chlorate, treated with tartaric acid, and made barely alkaline with potassium hydroxide. The sulphides of lead, iron, copper, and bismuth were then thrown out by hydrogen sulphide, dissolved in nitric acid, and the solution was evaporated with hydrochloric acid to the expulsion of nitric acid. Iron was separated by a second hydrogen sulphide precipitation in acid solution, followed by filtration, and precipitation by ammonia in the oxidized filtrate. The ignited oxide was corrected for silica. The sulphides of lead, bismuth, and copper were dissolved in nitric acid, fumed with sulphuric acid, diluted, and filtered to remove lead. Bismuth was separated in the filtrate by precipitation with ammonium hydroxide, and determined by dissolving the precipitate in nitric acid, precipitating as the oxy-nitrate and igniting to Bi_2O_3 . Copper was determined by electrolysis of the acidified ammoniacal filtrate from the bismuth.

Determination of lead.—The sample was dissolved in tartaric acid and nitric acid, and most of the lead separated as the sulphate by the addition of sulphuric acid followed by boiling to complete expulsion of nitric acid, slight dilution, filtration, and washing with water. The lead sulphate was dissolved in ammonium acetate, the solution filtered, and the lead precipitated as the chromate. Lead was calculated on the basis of the factor 0.64056. Lead was also recovered in the first filtrate and from the part insoluble in ammonium acetate by two alkaline sulphide separations, with filtration of the final insoluble sulphides, solution and electrolysis as PbO_2 .

Determination of antimony and tin.—The sample was dissolved in concentrated sulphuric acid, cooled, and treated with a solution of tartaric acid and concentrated hydrochloric acid and then gently boiled. The boiled solution was then cooled, diluted, treated with more hydrochloric acid, and titrated in ice-cold solution with permanganate.

Tin was determined iodimetrically in the above solution after adding more hydrochloric acid and reducing with antimony in an atmosphere of carbon dioxide.

Determination of arsenic.—The sample was dissolved in concentrated sulphuric acid, treated with concentrated hydrochloric acid and ferrous sulphate, and then distilled. Arsenic was then thrown out from the distillate as impure sulphide, which was weighed, treated with ammonium carbonate to dissolve the arsenious sulphide, and the residue reweighed.

(3) Lead and bismuth were determined as by Analyst 1. Tin was determined by Low's method, with reduction by iron-wire nails. Arsenic and copper were determined by Thompson's method.¹ Antimony was determined by the above method and also by direct titration as in Low's method. Iron was determined by an ammonium sulphide separation from the filtrate from the lead sulphate as obtained according to the "Methods of the U. S. Steel Corporation for Ferro Alloys and Bearing Metals," followed by reduction with zinc and titration with permanganate.

¹ G. W. Thompson, J. Soc. Chem. Ind., 15, 179. Proceedings Am. Soc. Testing Mat., 20 (1920), pages 589-594.

dissolved in hydrochloric acid, and fumed to zinc sulphate with sulphuric acid. (6) As zinc oxide. (7) As pyrophosphate. (8) Electrolyte made alkaline, then acid with formic acid, and zinc sulphide precipitated. Ignited at 850°-900°, weighed, and corrected for material insoluble in hydrochloric acid (1:1). (9) Filtrate from nickel determination fumed with sulphuric acid, diluted, treated with hydrochloric acid and ammonium chloride and titrated with ferrocyanide with ammonium molybdate as indicator. (10) As pyrophosphate in acetic acid solution after nickel separation with glyoxime. (11) Separated as sulphide in very dilute sulphuric acid, dissolved in hydrochloric acid, and titrated with ferrocyanide. (12) Combined sodium hydroxide filtrates from the nickel determination as above electrolyzed. (13) Sodium hydroxide filtrates from determination of nickel *b* treated with sodium hydroxide and Rochelle salts and electrolyzed. Corrected by a blank run under same conditions. (14) *a*. Precipitated as phosphate, dissolved in hydrochloric acid, neutralized with sodium hydroxide and electrolyzed (1.73%). *b*. Zinc determined as pyrophosphate (1.93%). (15) As pyrophosphate in filtrate from nickel.

LEAD

(1) *a*. Simultaneous electrolysis with copper in solution obtained as for copper above. Conversion factor for PbO_2 .866 used. *b*. Determined as sulphate in solution obtained as for copper above, and residual lead subsequently recovered on anode during copper determination. (2) *a*. Main solution with recovery from tin and antimony electrolyzed and factor 0.8643 used. *b*. Main solution with recovery treated with 40 cc of "lead acid" (300 cc H_2SO_4 , sp. gr. 1.84, and 1800 cc H_2O treated with 1 g $Pb(C_2H_3O_2)_2$ dissolved in 300 cc H_2O , and filtered after 24 hours) evaporated to appearance of fumes, diluted to 40 cc, and digested cold before filtration. (3) By electrolysis. (4) Electrolysis as under copper. (5) Electrolysis as under copper. (6) *a*. Electrolysis. *b*. As chromate. (7) Electrolysis as under copper. (8) As lead sulphate with recovery on anode during copper electrolysis and also by hydrogen sulphide in electrolyte. (9) Electrolysis with copper. (10) *a*. Electrolysis. *b*. Electrolysis followed by solution and precipitation as sulphate. (11) Separated as sulphate, dissolved in ammonium acetate, precipitated and weighed as chromate. Theoretical factor employed. (12) Simultaneously electrolyzed with copper as above. (13) As in (12). Factor 0.8643 used. (14) *a*. Separated as sulphate, dissolved in ammonium acetate, precipitated and weighed as molybdate. *b*. As $PbSO_4$ with subsequent recovery during electrolysis for copper. (15) As $PbSO_4$ after separation of tin and antimony.

ANTIMONY

(1) Nitric acid attack, solution of tin and antimony in a Kjeldahl flask in sulphuric acid and potassium sulphate, treatment with a little sodium sulphite, expulsion of sulphur dioxide fumes, and titration with permanganate after addition of hydrochloric acid. (2) *a*. Ammonium sulphide filtrate obtained as in copper above oxidized with hydrogen peroxide and antimony thrown out by hydrogen sulphide in presence of oxalic acid. Sulphide dissolved in nitric and sulphuric acids, nitric acid evaporated, solution diluted, filtered, antimony sulphide again thrown out and ignited at not over 950° to Sb_2O_4 (.19%). *b*. Nitric acid attack, solution of tin and antimony in nitric acid, ammonium persulphate and sulphuric acid, followed by evaporation to appearance of fumes. Diluted solution treated with hydrochloric acid, cooled, titrated with permanganate to a pink tint, ferrous sulphate added with back titration (.16%). (3) Precipitation as sulphide, oxalic acid separation from tin. (4) Antimony separated by sodium hydroxide-sodium sulphide and electrolyzed. Deposit dissolved in concentrated sulphuric acid, diluted and titrated with permanganate. (5) Nitric acid attack, followed by sulphuric acid and potassium sulphate, solution diluted and titrated with permanganate after addition of hydrochloric acid. (6) By titration. (7) Volumetrically on separate sample. (8) As analyst 1. (9) As analyst 1, except that tartaric acid was used and the sulphuric acid nearly all expelled. (10) Volumetrically with permanganate. (11) Oxides of antimony and tin fused with carbonate and sulphur. Filtrate oxidized with hydrochloric acid and chlorate, neutralized with ammonia, treated with oxalic acid, and antimony precipitated with hydrogen sulphide. Antimony sulphide dissolved in potassium sulphide, oxidized with chlorate and hydrochloric acid; solution boiled and titrated with thiosulphate. (12) Matter insoluble in nitric acid dissolved in sulphuric acid and potassium sulphate. Solution treated with 0.5 g tartaric acid and heated to complete decomposition; final permanganate titration after dilution and addition of hydrochloric acid. (13) Filtrate from carbonate-sulphur purification of tin treated with oxalic acid, saturated with hydrogen sulphide, and filtered precipitate washed with alcohol, carbon bisulphide, alcohol, and ether, dried in an atmosphere of carbon dioxide, first at 265° F. and then at 570° F. and weighed as Sb_2S_3 . (14) Matter insoluble in nitric acid digested with sulphuric acid, potassium sulphate and tartaric acid and titrated with permanganate after addition of hydrochloric acid. (15) Alkaline sulphide filtrate from fusion acidified, sulphides dissolved in hydrochloric acid, solution neutralized with ammonia, and antimony sulphide precipitated in oxalic acid solution. Sulphide dissolved and titrated with iodine in bicarbonate solution.

NICKEL

(1) Determined as glyoxime in the combined filtrates from the iron determination. (2) Combined filtrates from iron treated with glyoxime, precipitate dissolved in hydrochloric acid, reprecipitated as glyoxime, this again dissolved in hydrochloric acid, and evaporated with sulphuric acid to appearance of fumes; finally electrolyzed after addition of ammonia. Slightly higher values were obtained by this method than by direct weighing of the glyoxime. (3) As glyoxime. (4) Electrolyte from copper and lead treated with citric acid, ammonium chloride, glyoxime and

finally ammonia. Precipitate after short digestion, filtered, dissolved in hydrochloric acid, reprecipitated and weighed as glyoxime. (5) Filtrate from the zinc determination boiled, made slightly alkaline with ammonia, precipitated with glyoxime and weighed. (6) Glyoxime method. (7) Glyoxime method. (8) As glyoxime in combined filtrates from iron separation. (9) As glyoxime in filtrates from the iron determination. (10) As glyoxime after separation of iron. Weighed on counterpoised filters and checked by ignition to oxide. (11) As glyoxime in filtrate from zinc determination. (12) Electrolyte fumed with sulphuric acid, poured into sodium hydroxide solution, filtered, precipitate dissolved in dilute sulphuric acid and again precipitated. Nickel hydroxide then washed and ignited to NiO. (13) *a.* Glyoxime precipitation in combined filtrates from the iron determination (.12%). *b.* Combined filtrates from iron fumed with sulphuric acid, boiled with sodium hydroxide to expulsion of ammonia, and oxidized with bromine water. Precipitate filtered off, dissolved in hydrochloric acid, solution boiled to expel bromine, neutralized with ammonia added in excess, electrolyzed, deposit weighed, dissolved, and again electrolyzed for copper correction (.08%). (14) As glyoxime in electrolyte after removal of iron. (15) As glyoxime after iron separation.

IRON

(1) Filtrate from the zinc determination boiled, oxidized with nitric acid, precipitated twice with ammonia, and the precipitate ignited and corrected for silica. (2) Main filtrate with recovery from tin and antimony evaporated with sulphuric acid to appearance of fumes, diluted, and lead filtered off. Copper removed by electrolysis, and iron precipitated twice by ammonia in electrolyte. Iron hydroxide dissolved in sulphuric acid, reduced in reductor and titrated with permanganate. (3) Permanganate titration. (4) Iron determined volumetrically with permanganate after removal of the sulphide group. (5) Sample dissolved in aqua regia, precipitated with ammonia and the precipitate treated with sulphuric acid. Hydrogen sulphide group separated, filtrate boiled, reduced and titrated with permanganate. (6) Colorimetrically. (7) Precipitated by ammonia, dissolved and determined volumetrically. (8) Weighed as oxide after double precipitation of electrolyte with ammonia. (9) Determined by double ammonia precipitation of electrolyte, followed by solution in hydrochloric acid, reduction with stannous chloride, and final titration with permanganate. (10) As oxide from electrolyte, and including recovery from tin and antimony. (11) Sample dissolved in nitric and sulphuric acids, electrolyzed without filtration and electrolyte boiled with hydrochloric acid. Sulphide group removed, filtrate oxidized and treated with ammonia. Precipitate fumed with nitric and sulphuric acids, traces of lead filtered off and solution reduced in reductor and titrated with permanganate. (12) Main nitric acid filtrate with recovery of iron from tin and antimony precipitated with ammonia. Precipitate dissolved in dilute sulphuric acid, reduced in a reductor and titrated with permanganate. (13) Electrolyte with recovery of iron from tin and antimony precipitated twice with ammonia. Precipitate weighed as Fe_2O_3 after silica correction. (14) Ammonia precipitate of electrolyte ignited to Fe_2O_3 and corrected for silica. (15) Ammonia precipitation of electrolyte, solution of precipitate in sulphuric acid, reduction in reductor and titration with permanganate.