

DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 54

TIN-BASE BEARING METAL

SAMPLE PREPARED BY THE NATIONAL LEAD COMPANY, BROOKLYN, N. Y.

| Analyst | Tin | Antimony | Copper | Lead | Iron | Bismuth | Arsenic |
|---------------|-------|----------|--------|------|-------|---------|---------|
| 1..... | 88.17 | 7.31 | 3.77 | 0.55 | 0.06 | 0.06 | 0.05 |
| 2..... | 88.40 | 7.27 | 3.78 | 0.55 | 0.067 | 0.055 | 0.056 |
| 3..... | 88.23 | 7.25 | 3.76 | 0.57 | 0.10 | 0.06 | 0.04 |
| 4..... | 88.09 | 7.38 | 3.75 | 0.57 | 0.06 | 0.06 | 0.04 |
| 5..... | 88.20 | 7.32 | 3.76 | 0.58 | 0.044 | 0.042 | 0.053 |
| 6..... | 88.34 | 7.21 | 3.78 | 0.54 | 0.03 | 0.06 | 0.06 |
| 7..... | 88.14 | 7.39 | 3.82 | 0.56 | 0.06 | 0.04 | 0.07 |
| 8..... | 88.43 | 7.48 | 3.61 | 0.50 | 0.04 | 0.04 | 0.06 |
| 9..... | 88.10 | 7.34 | 3.78 | 0.60 | 0.05 | 0.066 | 0.05 |
| 10..... | 88.45 | 7.27 | 3.69 | 0.54 | 0.056 | | Trace. |
| 11..... | 88.18 | 7.30 | 3.74 | 0.57 | 0.063 | 0.042 | 0.054 |
| 12..... | 88.10 | 7.39 | 3.78 | 0.61 | 0.09 | 0.04 | 0.02 |
| Averages..... | 88.24 | 7.33 | 3.75 | 0.56 | 0.06 | 0.05 | 0.05 |

0.04 per cent of carbon was reported by analyst 12.

INDEX TO ANALYSTS

- | | |
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| <ol style="list-style-type: none"> 1. J. A. Scherrer, Bureau of Standards, Washington, D. C. 2. Edgar Cornell, jr., Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa. 3. H. W. Maack, S. Wilner, and E. W. Hutchison, Crane Co., Chicago, Ill. 4. F. M. Barry and L. E. Lougee, Scovill Manufacturing Co., Waterbury, Conn. 5. J. B. Mosley, The Ajax Metal Co., Philadelphia, Pa. 6. A. Craig, Ledoux & Co., 99 John Street, New York City. | <ol style="list-style-type: none"> 7. H. A. Bedworth, The American Brass Co., Waterbury, Conn. 8. W. J. Brown, National Lead Co., Brooklyn, N. Y. 9. Pennsylvania System, Dr. M. E. McDonnell, Chief Chemist, Altoona, Pa. 10. The Baldwin Locomotive Works, Philadelphia, Pa. 11. R. E. Maeder, The National Cash Register Co., Dayton, Ohio. 12. S. A. Weigand, The Lunkenheimer Co., Cincinnati, Ohio. |
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F. C. BROWN,
Acting Director.

Washington, D. C.
February 2, 1923.

**OUTLINES OF THE METHODS USED IN THE ANALYSIS OF THE BUREAU OF STANDARDS TIN-BASE
BEARING METAL STANDARD SAMPLE NO. 54**

METHODS EMPLOYED AT THE BUREAU OF STANDARDS

Determination of Tin

0.3 g of the alloy was dissolved in 12–15 cc of concentrated sulphuric acid, the solution diluted to 250 cc and treated with 80 cc of concentrated hydrochloric acid. The tin was then reduced by boiling for 30–45 minutes with test lead in an atmosphere of carbon dioxide, the solution cooled to 10° C, and titrated with iodine in the presence of carbon dioxide. The iodine solution was standardized under the same conditions against pure tin.

Determination of Antimony

2 g of the alloy was dissolved in 15–25 cc of concentrated sulphuric acid, the solution diluted to 50 cc, reduced with sulphite and boiled to expel all sulphur dioxide. The solution was then diluted to 250 cc, treated with 20 cc of concentrated 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 permanganate solution was standardized against pure antimony.

Determination of Arsenic

Arsenic was distilled from a 10-g portion and then precipitated as the sulphide. This was dissolved in ammonia, the arsenic oxidized by nitric acid, and precipitated as silver arsenate, which was washed, dissolved, and titrated as in Volhard's method.

Determination of Bismuth, Iron, Copper, and Lead

10 g of the alloy was dissolved in aqua regia, oxides of nitrogen were driven off, and the solution was diluted and made alkaline with potassium hydroxide added in a 5–10 g excess. After dilution to 500 cc, the solution was treated with a rapid stream of hydrogen sulphide for 15 minutes, digested on the steam bath for 2–3 hours, and finally allowed to stand at room temperature overnight. The solution was then filtered, the sulphides were washed moderately with 1–2 per cent potassium sulphide solution, and the filtrate was discarded. The sulphides were dissolved in aqua regia and reprecipitated and washed as above. The purified sulphides were dissolved in nitric acid, and the bismuth separated as the oxychloride. Bismuth was finally weighed as Bi_2O_3 after dissolving the oxychloride in hydrochloric acid, precipitating the bismuth with hydrogen sulphide, dissolving the sulphide in nitric acid, precipitating as basic carbonate with ammonium carbonate, dissolving the precipitate in nitric acid, evaporating the solution to dryness, and finally igniting to oxide. The filtrate from the hydrogen sulphide precipitation of bismuth was reserved on account of its iron content. The filtrate from the oxychloride precipitation was acidified, treated with hydrogen sulphide, and the sulphides were filtered off and washed with acidulated hydrogen sulphide water. This filtrate, combined with the one reserved above, was used for the determination of iron as oxide corrected for silica. The sulphides were dissolved in nitric acid and electrolyzed for copper and lead.

METHODS EMPLOYED BY THE COOPERATING ANALYSTS
(Numbers correspond to analysts on the certificate)

2. Tin was determined by iodine titration on a 0.5-g sample and the analyst stated that no success was had with gravimetric methods. Antimony was determined by Low's method on a 1-g sample. Bismuth was weighed as Bi_2O_3 , iron was determined as Fe_2O_3 , copper was determined electrolytically, and lead was obtained by electrolysis (0.50 per cent) and by the gravimetric method as sulphate (0.54 per cent). Arsenic was distilled and weighed as sulphide. All of the minor constituents were determined on 10-g samples.

3. Tin was determined iodimetrically on a 0.5-g sample essentially as in the Bureau method. Antimony was obtained by digestion of a 2–3-g sample with nitric acid with a recovery of antimony in the nitric acid filtrate by treatment with ammonium sulphide in excess, followed by filtration and acidification of the filtrate. The combined residues were dissolved by digestion with sulphuric acid and potassium sulphate in a Kjeldahl flask and antimony then determined as in the Bureau method. Arsenic was distilled at not over 108° C, the distillate treated with sodium bicarbonate in excess and then titrated with iodine. Bismuth was separated as sulphide by treating 5–10 g of the alloy essentially as in the Bureau method except that sodium sulphide was used instead of hydrogen sulphide. The sulphide was first digested with potassium cyanide solution to remove copper, then dissolved in nitric acid and treated to precipitate bismuth as oxychloride. The oxychloride was dissolved in nitric acid and the bismuth precipitated as basic carbonate and treated as in the Bureau method. For the determination of lead, copper, and iron, 3 g of the alloy was digested with nitric acid and the solution filtered. The insoluble matter was dissolved as in the antimony determination and any iron, etc., recovered by treatment with potassium sulphide and solution of the insoluble sulphides in nitric acid. The lead was finally determined as sulphate; copper was determined electrolytically with correction for any which was undeposited. Iron was precipitated as hydroxide, reduced with stannous chloride and titrated with permanganate.

4. Tin was determined by Thompson's method ¹ (88.01 per cent) and by Stief's method ² (88.17 per cent). Antimony was determined by Thompson's method (7.45 per cent) and by Stief's method (7.31 per cent). Arsenic was determined as in Thompson's method, except that the alloy was first put in solution with concentrated sulphuric

¹ G. W. Thompson, *J. Soc. Chem. Ind.*, 15, 179; *Proceedings A. S. T. M.*, 20, 589–94 (1920).

² F. A. Stief, *J. I. E. C.*, 7, 211 (1915); *Proc. A. S. T. M.*, 20, 596–7 (1920).

acid (sp. gr. 1.84) and a double distillation was carried out. Lead was separated by Thompson's method and finally determined by the electrolytic method together with copper. Bismuth and iron were obtained by dissolving a 10-g sample in hydrochloric acid and potassium chlorate and extracting with potassium sulphide in excess. The sulphides were dissolved in nitric acid, bismuth was separated as the oxychloride, and iron precipitated as hydroxide, which was then dissolved, reduced, and titrated with permanganate.

5. Tin was separated as metastannic acid by a nitric acid attack on a 1-g sample. The separated metastannic acid was dissolved by digestion with sulphuric acid and potassium sulphate and the solution diluted to 1 liter. One hundred cc of this solution was treated with hydrochloric acid, reduced under carbon dioxide with powdered antimony, and then titrated with iodine solution. Antimony was determined essentially as in the Bureau method. Arsenic was distilled from a 5-g sample and precipitated as As_2S_3 . For the determination of copper, lead, and bismuth, a 5-g portion of sample was dissolved in aqua regia, treated with an excess of sodium sulphide and hydroxide, and the sulphides were dissolved in nitric acid. Bismuth was then separated as the oxychloride, reprecipitated as the basic carbonate and ignited to Bi_2O_3 , while copper and lead were determined electrolytically. Iron was determined by dissolving 10 g of the sample in aqua regia, diluting the solution to 2 liters, precipitating with hydrogen sulphide, and filtering. The filtrate was evaporated after the addition of nitric acid, the iron separated as the hydroxide and determined by reduction in a Jones reductor and titration with permanganate.

6. For the determination of tin, 0.35 g of sample was treated with nitric acid, the metastannic acid filtered off, fused with sodium peroxide, and the tin determined iodimetrically after reduction with nickel in an atmosphere of carbon dioxide. Arsenic was distilled and weighed as As_2S_3 . Antimony was separated together with copper, arsenic, bismuth, and some lead by solution of the alloy in aqua regia, evaporation to dryness, extraction with potassium hydroxide solution, and precipitation with hydrogen sulphide after the addition of oxalic acid and ammonium oxalate. The sulphides were leached with a solution of potassium hydroxide, potassium sulphide, and potassium sulphate and the dissolved sulphides reprecipitated with hydrochloric acid. The mixed sulphides of antimony, arsenic, and part of the tin were dissolved in hydrochloric acid and potassium chlorate, the solution was boiled to expel chlorine, reduced with sulphur dioxide, and antimony determined by titration with potassium bromate solution. Copper and bismuth were obtained in the insoluble sulphides left after separating antimony, etc. These were dissolved in nitric acid, the lead was separated as sulphate, and copper and bismuth were thrown out electrolytically and weighed. The cathode deposit was dissolved, bismuth separated by precipitation with ammonia and ammonium carbonate, reprecipitated as $BiOCl$, weighed, and the bismuth so found deducted from the cathode weight. Bismuth was also obtained by dissolving 5 g of sample in aqua regia, making the solution alkaline with ammonia, adding potassium cyanide until the solution cleared, and then adding NH_4HS . Bismuth, lead, and iron were thus separated as sulphides, which were filtered off, washed with dilute NH_4HS , dissolved in nitric and sulphuric acids, and lead was separated as the sulphate which was converted to the chromate and weighed. The bismuth in the filtrate was reprecipitated as sulphide, dissolved in nitric acid, and converted to $BiOCl$ and weighed. Lead and iron were determined by dissolving 5 g of sample in aqua regia, adding tartaric acid, ammonia in excess, and then hydrogen sulphide. The sulphide precipitate was washed with ammonium sulphide plus ammonia, dissolved, and the treatment repeated. The purified sulphides were dissolved, lead was separated as sulphate, the sulphate dissolved in nitric and sulphuric acid, reprecipitated, dissolved in ammonium acetate and precipitated and weighed as chromate. Iron was found in the combined filtrates from the lead separations by first treating the acid solution with hydrogen sulphide, filtering, oxidizing the filtrate, precipitating iron with ammonia, and then dissolving the hydroxide in sulphuric acid, reducing in a reductor, and oxidizing with permanganate.

7. Tin was determined iodimetrically. Antimony was determined volumetrically as in the Bureau method. Arsenic was distilled and the distillate titrated with iodine. Iron was separated as in the Bureau method and then determined volumetrically by titration with permanganate. Copper and lead were determined by Thompson's method,¹ except that the preliminary alcohol separation was omitted and the solution directly evaporated to dryness; lead was separated as sulphate and bismuth as basic carbonate before the electrolysis for copper. Bismuth was separated as in the Bureau method, and determined by dissolving the basic carbonate and proceeding by Ferguson's colorimetric method.²

8. Tin was determined by Thompson's method (88.44 per cent) and also by the iodimetric method (88.42 per cent). Antimony and copper were determined by Thompson's method. Lead was determined by Thompson's method (0.35 per cent), and also by first separating the lead as sulphide, then as sulphate, and finally weighing as chromate. Arsenic was separated by distillation and weighed as sulphide.

9. Tin was determined gravimetrically by treating 0.5 g of the sample with nitric acid, evaporating the solution to dryness, taking up in dilute nitric acid, digesting the solution, and finally filtering, igniting, and weighing the impure metastannic acid. The impurities were then separated by a sodium carbonate-sulphur fusion treatment, and these, together with antimony as separately determined, deducted. Antimony was determined gravimetrically by dissolving 1 g of sample in aqua regia, making the solution alkaline and then separating antimony from tin by adding oxalic acid, ammonium oxalate, and hydrogen sulphide. The sulphides were dissolved in potassium hydroxide, the solution was treated with an excess of hydrochloric acid and evaporated to eliminate arsenic. After oxidizing

¹ Loc. cit.

² Scott, *Standard Methods of Chemical Analysis*, 2d Ed., p. 69.

the solution with potassium chlorate, the antimony was again precipitated as sulphide as above. The antimony sulphide was then filtered on a platinum gooch crucible with asbestos pad, washed with hot water, alcohol, carbon disulphide, alcohol, and ether and dried in an atmosphere of carbon dioxide at 265° F for one hour and then at 570° F to constant weight of Sb_2S_3 . Arsenic was obtained on a 5-g sample by dissolving in sulphuric acid, distilling after adding hydrochloric acid and ferrous sulphate and precipitating arsenic as the sulphide, which was washed with hot water, alcohol, carbon disulphide, alcohol, and dried at 212° F to constant weight. The weighed sulphide was treated with a warm solution of ammonium carbonate, washed with water and alcohol, again dried and reweighed. For iron, bismuth, copper, and lead a 2-g sample was dissolved in aqua regia, treated with potassium chlorate, and then with tartaric acid, potassium hydroxide, and hydrogen sulphide. The sulphides were dissolved in nitric acid and reprecipitated as above. The purified sulphides were dissolved and the acid solution was treated with hydrogen sulphide to separate iron. The hydrogen sulphide filtrate was oxidized, iron precipitated by ammonia, and ignited to oxide, which was corrected for silica. The sulphides of bismuth, copper, and lead were dissolved, evaporated to the appearance of fumes with sulphuric acid, and lead was separated and weighed as sulphate. Bismuth was precipitated in the sulphuric acid solution by means of ammonia, and separated as the oxynitrate by dissolving the hydroxide in nitric acid and evaporating to sirup consistency several times with intervening additions of water. The oxynitrate was washed with dilute ammonium nitrate, ignited, and weighed as Bi_2O_3 . Copper and residual lead were obtained by electrolysis after combining the filtrate from the first bismuth precipitation with that from the final precipitation, evaporating, and adding nitric acid.

10. Tin was obtained by both volumetric and gravimetric methods. Antimony was obtained volumetrically by Low's modified method. Copper and lead were obtained by electrolysis and lead was checked by determination as sulphate. Iron was obtained by dissolving the alloy in aqua regia, diluting the solution to 1000 cc, precipitating with hydrogen sulphide, and then evaporating the filtrate, oxidizing with nitric acid, precipitating with ammonia, and igniting to Fe_2O_3 .

11. Tin and antimony were separated from a 5-g sample by solution in aqua regia, oxidation with potassium chlorate and treatment with tartaric acid, sodium hydroxide in excess, and sodium sulphide. Tin was separated from antimony by treating the filtrate obtained above with oxalic acid, boiling to complete solution, and then precipitating with hydrogen sulphide. The precipitate of antimony sulphide was dissolved and retreated as above, and tin then obtained in the combined filtrates by evaporating to smaller volume and electrolyzing (88.13 per cent). Tin was also obtained iodimetrically by dissolving 0.3 g of sample in an Erlenmeyer flask containing 5 g of iron wire and 75 cc of hydrochloric acid. The flask was fitted with a rubber stopper carrying a glass tube which dipped in dilute solution of sodium carbonate. The alloy was dissolved by heating gently at first and finally boiling. When solution was complete, the tube was immersed in strong carbonate solution, the flask allowed to cool, and the cooled solution treated with 200 cc of cold water and titrated with an iodine solution which had been standardized by the above procedure against pure tin plus antimony equivalent to that in the sample. Arsenic was distilled and weighed as As_2S_3 .¹ Copper, lead, bismuth, and iron were separated as sulphides by the double alkaline sulphide treatment described above. The sulphides were dissolved in nitric acid, the solution was neutralized with sodium carbonate and treated with potassium cyanide to separate lead and bismuth as carbonates. The carbonates were dissolved in nitric acid and bismuth was separated and weighed as $BiOCl$. The filtrate from the lead and bismuth carbonates was acidified with sulphuric acid and boiled (in the hood) to drive off cyanide, and then electrolyzed for copper. For lead, the sulphides which had been separated from tin and antimony were dissolved in nitric acid and electrolyzed. Iron was separated from the electrolyte by precipitating with ammonia and then determined gravimetrically and volumetrically.

12. For the determination of antimony, 1 g of the sample was dissolved in 20 cc of concentrated sulphuric acid in a 500-cc Florence flask, diluted to 200 cc with water, treated with 20 cc of concentrated hydrochloric acid, heated to boiling, cooled to 10° C and then titrated with a standard permanganate solution. Tin was determined by iodimetric titration of the same solution after adding 80 cc of concentrated hydrochloric acid, reducing under carbon dioxide by boiling for about one-half hour with 15 g of test lead, cooling to 10°, and titrating in the presence of carbon dioxide. Tin was also determined gravimetrically by dissolving 1 g of the sample in 10 cc of concentrated nitric acid, evaporating to dryness, and baking. The baked residue was moistened with nitric acid, taken up in 100 cc of boiling water, filtered, and the residue ignited and weighed. The impure residue was fused with carbonate and sulphur, and treated as usual for a recovery of the impurities. Copper, lead, bismuth, and iron were obtained essentially as in the Bureau method. Arsenic was distilled and then precipitated and weighed as As_2S_3 . Carbon was obtained by dissolving 5 g of the alloy in 50 cc of hydrochloric acid (1 : 1) in the cold. The solution was then filtered on an asbestos pad, and the carbon determined by combustion.

¹ A. S. T. M. Proc. XIX (1919), Part 1, p. 512.