

U. S. DEPARTMENT OF COMMERCE

National Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE 124

OUNCE METAL

Analyst*	Copper	Zinc	Lead	Tin	Nickel	Iron	Antimony	Silicon	Sulfur	Phosphorus	Aluminum	Arsenic
1.....	83.79	5.45	^a 4.78	^b 4.69 ^c 4.59	0.45	0.37	^b 0.23 ^c 0.24	0.080	0.067	0.034	^d 0.015 ^e 0.016	Not detected.
2.....	83.75	5.44	^f 4.76	^b 4.69 ^c 4.64	.45	.38	^b .22 ^c .26	.077	.073	.037		
3.....	83.75	^g 5.47	^h 4.78	ⁱ 4.73	.45	.37	ⁱ .22	^k .073	.074	.039	^d .015	
4.....	83.71	5.57	4.72	4.61	.46	.39	.23	.063	.071	.038	.020	
5.....	83.80	5.47	^a 4.76	^l 4.70	.45	.36	^l .24	.074	.071	.038	.020	
6.....	83.75	5.45	4.82	4.72	.45	.36	.22	.077	.076	.037	.018	
7.....	83.72	5.40	^a 4.81	^m 4.78	.43	.40	ⁿ .25	^o .063	^p .064	.033	^e .016	
8.....	^q 83.82	^r 5.39	^a 4.81	4.69	^r .43	^a .38	ⁿ .23	.073	.070	.032	^e .014	
9.....	83.74	5.51	^a 4.71	4.75	.44	.38	.23	.065	.079	.039	.020	
10.....	83.84	5.43	4.85	4.69	.45	.38	.23	.065	.065	.040	^d .020	
Averages.....	83.77	5.46	4.78	4.69	0.45	0.38	0.23	0.071	0.071	0.037	0.017	
Recommended values.....	83.77	5.46	4.78	4.69	0.45	0.38	0.23	0.075	0.071	0.037	0.016	

^a Weighed as PbSO₄.

^b Distillation method, see methods used at NBS.

^c Direct method, see methods used at NBS.

^d Colorimetric with aurintricarboxylate.

^e Weighed as AlPO₄.

^f Electrolytic, weighed as PbO₂.

^g Finished by electrolysis.

^h Same value by sulfate and electrolysis.

ⁱ 2-g. sample dissolved in aqua regia. Solution treated with an excess of NH₄OH, filtered, and precipitate digested in H₂SO₄-K₂SO₄. Tin reduced with metallic antimony and titrated with KIO₃.

^j Metastannic acid and the like separated and digested in H₂SO₄-K₂SO₄. Solution diluted, reduced with tartaric acid and Sb titrated with KMnO₄.

^k Five 2-g. samples dissolved in aqua regia, 10 ml. of H₂SO₄ added and solution evaporated to copious fumes of H₂SO₄. Residue treated with 150 ml. of diluted HCl (1+9). Solutions filtered through same paper, washed with HCl (1+9), ignited and treated with HF.

^l Metastannic acid and the like separated and digested in H₂SO₄-K₂SO₄. Solution diluted, reduced with Na₂SO₃, and Sb titrated with KMnO₄. Titrated solution reduced with test lead and tin titrated with iodine solution.

^m Metastannic acid and the like separated, digested, etc., and tin reduced with powdered antimony. Solution titrated with 0.01 N iodine.

ⁿ 5-g. sample treated essentially as in *j*.

^o Five 2-g. samples dissolved in 20 ml. of H₂O, 10 ml. HCl, 5 ml. of HNO₃, and 5 ml. of H₂SO₄. Solution fumed and determination completed as in *k*.

^p 5-g. sample dissolved in 10 ml. of HBr (48 percent) containing some SnCl₂. Evolved gases passed through an ammoniacal CdCl₂ solution. Solution acidified and titrated with 0.02 N iodine.

^q Copper, lead, and iron in metastannic acid recovered by sodium carbonate-sulfur fusion.

^r Nickel-dimethylglyoxime ignited to NiO.

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METHODS USED AT THE NATIONAL BUREAU OF STANDARDS IN THE ANALYSIS OF STANDARD SAMPLE OF OUNCE METAL No. 124

The methods used at the Bureau are longer and more involved than those used in commercial analyses. They were chosen on the basis of accuracy rather than on speed or simplicity.

Separation of copper, lead, zinc, iron, aluminum, and nickel from arsenic, antimony, tin, and phosphorus.—Dissolve a 5-g. sample in 50 ml. of nitric acid (1+1), boil, dilute to about 150 ml. with hot distilled water and digest on a steam bath for 2 to 3 hours, or preferably overnight. Filter the hot solution through a close-textured paper and wash with hot diluted nitric acid (1+99). Reserve the filtrate and washings (A), which should be clear. Transfer the filter paper and contents to a Kjeldahl flask, add 12 to 15 ml. of sulfuric acid (sp. gr. 1.84), and about 5 g. of pure sodium sulfate. Heat until all organic matter is decomposed. Transfer the digested solution to a 400-ml. beaker, dilute to 250 ml., and add (quantitatively) about 2 ml. of filtrate (A). Then add a solution of sodium hydroxide (25 to 30 percent) until the solution is alkaline and the tin hydroxide has dissolved. Add 20 ml. of a 25-percent solution of sodium sulfide, stir thoroughly, and digest on a steam bath for several hours or until the supernatant liquid is clear. Cool to room temperature, filter through a paper of close texture, and wash the precipitate with a 2-percent solution of sodium sulfide. In very accurate work, dissolve the sulfides and repeat the separation. Dissolve the final sulfides in diluted nitric acid (1+1), filter the solution, and add the filtrate to the reserved nitric-acid filtrate (A).

Determination of lead.—Add 10 ml. of sulfuric acid (sp. gr. 1.84), evaporate to fumes of sulfuric acid, cool, wash down the sides of the vessel with water, and again evaporate to fumes of sulfuric acid. Dilute to 150 ml., let stand for 1 to 2 hours, filter the cool solution through a tared Gooch crucible, and wash the precipitate with a cool diluted solution of sulfuric acid (3+97). Reserve the filtrate and washings. Heat the precipitate to constant weight at very dull redness (500° to 600° C.) by suspending the crucible in a larger crucible so that an air space separates the two. Calculate the percentage of lead from the weight of $PbSO_4$ obtained.

Determination of copper and residual lead.—Add 2 ml. of nitric acid to the reserved filtrate and washings, dilute to about 200 ml., and electrolyze overnight with weighed gauze electrodes at 0.5 ampere and 2 volts. Without interrupting the current, withdraw the electrolyte as the electrodes are well washed with water from a wash bottle. Reserve the electrolyte. Rinse the cathode in alcohol, dry it for a few minutes at 100° C., cool, and weigh the deposit of copper. Dry the anode at 180° C., cool, and weigh the PbO_2 and test it for impurities. Calculate lead by the factor 0.866 and add the recovery to the lead already found as sulfate.

Determination of zinc and residual copper.—Evaporate the electrolyte and washings to small volume and heat to the appearance of fumes of sulfuric acid. Cool, dilute to 200 ml., and treat with hydrogen sulfide. If a precipitate appears, filter, wash with diluted sulfuric acid (1+99) saturated with hydrogen sulfide, ignite at 900° to 1,000° C., and weigh as CuO . Test for impurities, such as tin and antimony, and make appropriate corrections for any elements found.

Boil the filtrate to expel hydrogen sulfide, add 2 drops of methyl orange solution, and neutralize with ammonium hydroxide. Finally, dilute to at least 100 ml. for every 0.1 g. of zinc and add 0.9 ml. of *N* sulfuric acid for each 100 ml. of solution. Cool to room temperature and precipitate zinc as sulfide, using a rapid current of hydrogen sulfide. Allow the precipitate to settle for about 30 minutes and then filter the solution through a paper of close texture. Wash with cold water, reserve the filtrate, and ignite the paper and contents very slowly in an oxidizing atmosphere until all carbon is destroyed. Gradually increase the temperature to 950° to 1,000° C., and heat at this temperature for about 25 minutes. Cool and weigh as ZnO .

Determination of iron.—Add 5 ml. of sulfuric acid to the filtrate reserved from the determination of zinc. Boil the solution until hydrogen sulfide is expelled, using a few milliliters of nitric acid, or a few crystals of ammonium persulfate at the end to eliminate sulfur and to oxidize the iron. Add a slight excess of ammonium hydroxide, boil the solution for 1 to 2 minutes, filter, and reserve the filtrate for the determination of nickel. Dissolve the precipitate in diluted hydrochloric acid, precipitate with ammonium hydroxide as before, filter, and wash with hot ammonium chloride solution (2 percent). Add this filtrate to the one already reserved. Dissolve the precipitate of iron hydroxide in diluted hydrochloric acid and dilute the solution to 200 ml. Add 5 g. of tartaric-acid crystals, stir, and reduce the acidity to about 2 percent by adding ammonium hydroxide. Pass a current of hydrogen sulfide through the solution for 10 to 15 minutes and filter if a precipitate appears. Add an excess of 5 ml. of ammonium hydroxide to the filtrate and treat with hydrogen sulfide for about 10 minutes. Filter the solution, dissolve the precipitate in hydrochloric acid, add 1 g. of tartaric acid, and precipitate with ammonium sulfide as before. Filter, dissolve the precipitate in hydrochloric acid, and oxidize the iron by adding nitric acid and boiling the solution.

Precipitate the iron with a slight excess of ammonium hydroxide, filter and wash. Ignite and weigh as Fe_2O_3 . Alternately, the ammonia precipitate can be dissolved, reduced, and titrated by the usual methods.

Determination of nickel.—Add a small excess of hydrochloric acid to the reserved filtrate, adjust the volume to 300 ml., add 0.5 g. of tartaric acid, and filter the solution if not absolutely clear. Nearly neutralize with ammonium hydroxide, warm, add a three- to five-fold excess of a 1 percent alcoholic solution of dimethylglyoxime, and make slightly ammoniacal. Digest for 1 hour at the side of the steam

bath. Cool, filter on a weighed close-frit glass crucible, and wash with cold water. Dry at 110° to 120° C. for about 2 hours, and weigh as the glyoxime salt, which contains 20.32 percent of nickel.

Determination of tin and antimony (distillation method).—Copper and lead were first separated from antimony and tin by electrolysis in a nitric-hydrofluoric acid solution. Antimony and tin in the electrolyte were converted to sulfates, separated by fractional distillation, and determined by titration. The following is an outline of the method: Place 3 g. of the sample in a 200-ml. platinum dish, provided with a platinum or gold cover, and add 50 ml. of water, 20 ml. of hydrofluoric acid, and 20 ml. of nitric acid (sp. gr. 1.42). When solution is complete, remove the cover, and evaporate on a steam bath to a volume of about 10 ml. Cool, add 10 ml. of hydrofluoric acid and 10 ml. of nitric acid (sp. gr. 1.42). Transfer the cold solution to a ceresin beaker and dilute to about 300 ml. Remove copper and lead by electrolysis, using gauze electrodes. Transfer the electrolyte to a platinum dish, add 10 ml. of sulfuric acid (sp. gr. 1.84), and evaporate the solution to fumes of sulfuric acid. Cool somewhat, wash down the sides of the dish, and again heat to fumes of sulfuric acid to expel any remaining hydrofluoric acid. Add about 0.2 g. of flowers of sulfur to the concentrated sulfuric-acid solution and boil gently for about 10 minutes to reduce antimony (and arsenic) to the trivalent state. Cool, add about 25 ml. of distilled water and 10 ml. of hydrochloric acid (sp. gr. 1.18). Stir to completely dissolve the compounds of antimony, tin, and arsenic. Immediately filter the solution through a paper of coarse texture and wash with about 20 ml. of diluted hydrochloric acid (1+1). Transfer the solutions to an all-glass distilling apparatus, wash the container with 40 ml. of hydrochloric acid (sp. gr. 1.18), and proceed with the distillation and determination of arsenic, antimony, and tin, as described in National Bureau of Standards Research Paper RP1116 (J. Research NBS vol. 21, p. 95, 1938).

Determination of tin and antimony (without distillation).—Place a 5 g. sample in a 400-ml. beaker, add 50 ml. of diluted HNO₃ (1+1), digest, and filter the residue of antimony, tin, etc., as described for the separation of copper, etc. Reserve the paper and contents. Add a moderate excess of ammonium hydroxide to the filtrate and boil the solution for several minutes. Filter and wash several times with warm diluted ammonium hydroxide (1+99). Transfer both papers and residues to the original beaker and add 10 ml. of sulfuric acid (sp. gr. 1.84) and 25 ml. of nitric acid (sp. gr. 1.42). Cover, and gently boil the solution until fumes of sulfuric acid are evolved. If the solution is brown, add more nitric acid and again evaporate to fumes of sulfuric acid. Cool, remove the cover, wash down the sides of the beaker, and evaporate to fumes of sulfuric acid to completely expel nitric acid. Add about 0.2 g. of flowers of sulfur to the concentrated sulfuric-acid solution and boil gently for about 10 minutes to reduce antimony to the trivalent state. Cool, add about 25 ml. of water, and boil until the volume of the solution is reduced by about one-half in order to expel sulfur dioxide. Cool, and add 30 ml. of diluted hydrochloric acid (1+2). Stir to completely dissolve the compounds of antimony, tin, and arsenic. Immediately filter the solution through a paper of coarse texture, catching the filtrate in a 500-ml. Erlenmeyer flask. Wash with 75 ml. of diluted hydrochloric acid (1+4) and then several times with warm water. Dilute the filtrate to 300 ml., boil for a few minutes, cool to about 10° C., and titrate with a standard solution of permanganate to a pink tint which persists for 10 seconds. Reserve the solution.

The permanganate solution is usually standardized by means of pure antimony. Arsenic interferes, and the apparent percentage of antimony is corrected by deducting 1.86 times the percentage of arsenic as separately determined.

To the titrated solution add 90 ml. of hydrochloric acid (sp. gr. 1.18) and 2 to 3 g. of test lead. Insert a three-hole stopper carrying gas inlet and outlet tubes and having the third hole closed by a small stopper. It is advisable to use an air condenser about 15 to 20 cm. in length in the gas outlet. Start a slow current of carbon dioxide from a Kipp generator or a cylinder, heat gradually to boiling, and boil gently for 30 to 40 minutes. Finally, cool in ice to about 10° C., after increasing the current of carbon dioxide to prevent back pressure. This may be detected by placing a bubble tube in the gas outlet. When the solution is cold, take out the stopper in the third hole, add 5 ml. of clear starch solution from a pipette, and insert the tip of a burette containing standard iodine solution and titrate to a permanent blue tint. The titration should be corrected by a blank determination (usually amounting to 0.05 to 0.08 ml. of 0.1 N iodine solution) carried through the steps of the procedure. The iodine solution should be standardized against pure tin by the method described, or a sample of ounce metal carried through all steps of the method, for the theoretical titre is usually a little low.

The determination of tin and antimony without separation by distillation tends to give slightly high results for antimony and slightly low results for tin (see NBS Research Paper RP1116).

Determination of silicon.—Dissolve a 5-g. sample in 50 ml. of nitric acid (1+1), digest, filter, and wash with diluted nitric acid (1+99), as described in the separation of copper, etc. Reserve the filtrate (A). Place the paper and precipitate in the original beaker, add 10 ml. of sulfuric acid (sp. gr. 1.84), stir, and let stand a few minutes. Add 25 ml. of nitric acid (sp. gr. 1.42), cover with a cover glass, and evaporate to fumes of sulfuric acid. Cool, add 10 ml. of nitric acid (sp. gr. 1.42), and again evaporate to fumes of sulfuric acid. Cool, dilute to 200 ml., add 10 ml. of hydrochloric acid (sp. gr. 1.18), and warm until salts are dissolved. Filter without delay and wash the paper and residue with diluted hydrochloric acid (1+99). Discard the filtrate and reserve the paper and precipitate.

Evaporate the reserved filtrate (A) just to dryness. Add 7 ml. of nitric acid (sp. gr. 1.42), 1 drop of 0.1 N hydrochloric acid, dilute to 225 ml. and electrolyze to remove copper and lead, using gauze electrodes. Add 10 ml. of sulfuric acid (sp. gr. 1.84) to the electrolyte and evaporate to copious fumes of sulfuric acid. Cool somewhat and cautiously add 10 ml. of diluted hydrochloric acid (1+1), and

then 175 ml. of water. Stir, and warm until salts are in solution. Filter and wash the paper and residue with diluted hydrochloric acid (1+99).

Transfer the two papers and residues to a platinum crucible, heat carefully until the carbon is gone and then cover and ignite for 15 to 20 minutes at 1,100° C. Cool in a desiccator and weigh. Add sufficient diluted sulfuric acid (1+1) to moisten the silica, and then 3 to 5 ml. of hydrofluoric acid. Evaporate to dryness, carefully heat to remove sulfuric acid, and then ignite at 1,000° C. Cool and weigh. The loss in weight multiplied by 46.72 and divided by the weight of sample represents the percentage of silicon. The result should be corrected by a blank run carried through all steps of the determination.

Determination of sulfur.—Transfer a 5-g. sample to a 250-ml. beaker and dissolve in a mixture of 40 ml. of equal parts of nitric acid (sp. gr. 1.42) and fuming nitric acid. When solution is complete, boil until oxides of nitrogen are expelled and dilute to 150 ml. with hot water. Digest on a steam bath for a few hours and filter while *hot* through a paper of close texture. Wash moderately with hot diluted nitric acid (1+99). The filtrates and washings should be perfectly clear. Evaporate the solution to dryness on a steam bath, add 7 ml. of nitric acid (sp. gr. 1.42), 1 drop of 0.1 N hydrochloric acid, and dilute to 225 ml. Electrolyze to remove copper and lead, using gauze electrodes. Complete deposition of lead is essential. Remove and wash the electrodes and then add 0.5 g. of sodium carbonate to the electrolyte. Evaporate the solution until nearly dry, add 20 ml. of hydrochloric acid (sp. gr. 1.18), and then evaporate to dryness. Again add 20 ml. of hydrochloric acid and evaporate to dryness. Add 2 ml. of hydrochloric acid (sp. gr. 1.18), 100 ml. of hot water, warm for a few minutes to dissolve soluble salts, and filter if any insoluble matter is present. Heat the filtrate to about 90° C. Add 10 ml. of a hot 10-percent solution of barium chloride, drop by drop, while stirring, and digest on the steam bath for 5 hours or longer. Cool, filter on a small paper of close texture, and wash with warm water until chlorides are removed. Transfer the paper and precipitate to a tared platinum crucible, heat in an oxidizing flame until carbon is destroyed, and then ignite at dull redness for 20 minutes. Cool and weigh as BaSO₄. Blank runs should be made and the results deducted, and great care must be exercised throughout to prevent contamination by sulfur from gas or fumes in the laboratory.

Determination of aluminum.—Transfer a 5-g. sample to a platinum dish, dissolve in nitric-hydrofluoric acids, and remove copper and lead by electrolysis as described in the determination of tin. Transfer the electrolyte to a platinum dish, add 7 ml. of sulfuric acid (sp. gr. 1.84), evaporate to fumes of sulfuric acid, and continue the heating for a few minutes. Cool somewhat, wash down the sides of the dish, and again heat to fumes of sulfuric acid to completely expel hydrofluoric and nitric acids. Cool, dilute to about 25 ml., and wash the solution into a Melaven mercury-cathode cell having a stirring arrangement. Electrolyze with a current of about 5 amperes until tin, zinc, iron, and the like are deposited in the mercury (about 1.5 to 2 hours). Transfer the electrolyte to a beaker, adjust the acidity to about 2 percent (by volume), and pass a current of hydrogen sulfide in the solution for about 10 minutes. Filter, and boil the filtrate until hydrogen sulfide is expelled. Cool the solution to about 50° C., add 5 ml. of hydrochloric acid (sp. gr. 1.18), and then 0.5 g. of (NH₄)₂HPO₄. Add a little ashless paper pulp, then 2 drops of methyl red indicator, and make just ammoniacal. Restore the pink color by adding diluted hydrochloric acid (1+20) dropwise. Heat the solution to boiling, and add 20 ml. of a 20-percent solution of NH₄C₂H₃O₂. Continue the boiling for 5 minutes, let settle (for 1 to 2 hours if the amount of aluminum is very small), and filter through a 9-cm. paper. Wash with a hot 5-percent solution of NH₄NO₃ until 5 ml. of the washings no longer give a test for chlorides with an acidified solution of AgNO₃. Ignite in platinum or porcelain under good oxidizing conditions until carbon is gone, cover, and heat at about 1,000° C. to constant weight. Weigh as AlPO₄ and correct for a blank carried through all steps of the method.

Alternately treat an aliquot portion (containing from 0.02 to 0.05 mg. of aluminum) of the electrolyte with 5 ml. of hydrochloric acid (sp. gr. 1.18), 5 ml. of glacial acetic acid, and 5 ml. of a 0.2-percent aqueous solution of a tested sample of ammonium aurintricarboxylate. Mix well while cautiously adding ammonium hydroxide until the cloudy appearance of the dye disappears and the solution becomes clear, although still acid to litmus. Place a piece of litmus paper against the inner surface of the beaker, and, while stirring the solution constantly, add ammonium hydroxide at a rate of about 1 drop every 2 seconds until about 2 ml. has been added; then add 1 drop every 3 or 4 seconds until the litmus paper turns blue. Now add 5 ml. of glacial acetic acid, let the solution stand for 10 minutes, and neutralize it as previously described. Finally, add 5 ml. of ammonium hydroxide. Cool to room temperature and compare with the color of standard aluminum solutions as described by J. A. Scherrer and W. D. Mogergerman, National Bureau of Standards Research Paper RP1117 (July 1938).

Determination of phosphorus.—Transfer 2 g. of the sample to a 300-ml. Erlenmeyer flask, and dissolve in a mixture of 15 ml. of nitric acid (sp. gr. 1.42) and 5 ml. of hydrochloric acid (sp. gr. 1.18). When solution is complete, add 20 ml. of hot water, digest it at 80° to 90° C. for 10 minutes, and dilute to 50 ml. Treat the hot solution with 100 ml. of molybdate reagent. Shake the solution for 10 minutes and allow to stand for at least 30 minutes. Filter, wash the flask, and precipitate with not more than 50 ml. of cold diluted nitric acid (1.5:98.5), added in 5-ml. portions, and then 10 times with 20-ml. portions of a 1-percent solution of potassium nitrate. Return the paper and precipitate to the original flask, dilute, and titrate with standard alkali and acid.

If desired, the phosphomolybdate can be dissolved in ammonium hydroxide and the phosphorus determined by weighing as Mg₂P₂O₇ following double precipitation with magnesia mixture and ignition.