

through for sulfur, using CuKBaCl solution and gave:

No.	Percentages sulfur	
	Fusion method	Vol. method
47006	0.136	0.114
47007	0.121	0.109
47008	lost	0.106

The filtrates from above stood on the oven for 4 days, then were filtered through paper and carefully washed with dilute HCl and water.

They weighed as follows:

47006.....	0.0014 gram
47007.....	0.0050 gram
47008.....	0.0025 gram

These tests deposited basic salts while standing on oven, to dissolve which they were treated twice with 2 cc. of HCl, but this did not prevent appearance of basic salts. On filtering no indication of BaSO₄ was noted and only an iron stain remained on paper. The 3 filter papers were ignited and weighed separately, then combined and fused with Na₂CO₃, the solution made faintly acid with HCl and evaporated to crystals. The residue was dissolved in 10 cc. of water and only a slight flocculent precipitate was visible (SiO₂?).

Effect of Hydrochloric Acid on the Solubility of Barium Sulfate

VIII—Four solutions were prepared, each containing 3 grams of sodium carbonate and sodium peroxide, made just acid to methyl orange with HCl. 5 cc. N/20 H₂SO₄ were added to each (=0.0294 gram BaSO₄).

HCl was added in increasing amounts to each test as follows:

	1	2	3	4
HCl.....	0.25 cc.	0.50 cc.	1.00 cc.	2.00 cc.

Tests were heated to boiling and slowly precipitated with 7 cc. hot BaCl₂ solution, using a Schuster bottle. Volume = 100 cc. All precipitates were granular and settled rapidly. All precipitates were collected on a carefully prepared asbestos pad and the following results were obtained:

	1	2	3	4
Gram BaSO ₄	0.0303	0.0304	0.0290	0.0312

184 WHITTIER AVE.
PROVIDENCE, R. I.

THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND COPPER

By D. J. DEMOREST

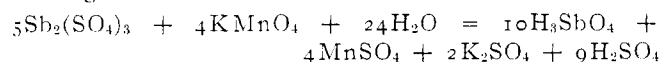
Received June 2, 1913

The following method of analysis has been devised after making hundreds of determinations on alloys and mixtures of metals. The earlier results were inaccurate but they showed the sources of error and ways for improvement in the manipulation until the method as here presented is, in the writer's opinion, the best method for obtaining quick and fairly accurate results in the analysis of the alloys of the above named metals.

The results obtained are reliable to within 0.2 per cent for lead, tin and antimony and 0.1 per cent for copper.

When fine shavings of an alloy containing any or all of the metals lead, tin, antimony, and copper are digested at a boiling heat with concentrated sulfuric acid, the lead is left insoluble as PbSO₄ while the tin goes into solution as Sn(SO₄)₂, copper as CuSO₄, and antimony as Sb₂(SO₄)₃. The lead sulfate is filtered off and weighed and the antimony in the filtrate is

titrated with standard permanganate solution according to the reaction:



After the antimony is titrated, the tin is reduced with iron in the presence of precipitated antimony and the stannous iron is titrated by standard iodine solution.

In another sample the lead is separated as above, and from the filtrate from the lead sulfate the copper is precipitated as CuCNS either with or without a previous titration of the antimony as the chemist may prefer. The CuCNS is then titrated with KMnO₄ or the copper is determined by the very accurate iodide method.

The new things about this method are: *First*, the titration of the antimony by permanganate in a sulfuric acid solution free from HCl; *second*, the combination of these four methods for lead, antimony, tin, and copper; and *third*, the manipulation necessary for the combination. A great many determinations were made before the manipulation necessary to obtain accurate results was worked out. It is necessary that the details as here given be strictly adhered to, but this is easily done.

Procedure.—Place 1 gram of fine shavings or drillings in a Kjeldahl flask with a short neck, and add 20 cc. of concentrated sulfuric acid. Heat nearly to boiling and continue the heating until the sample is nearly decomposed and the lead sulfate is white. This may take one-half hour. Finally boil for several minutes. Cool the solution and then add 50 cc. of water while the solution in the flask is kept agitated. Heat the liquid to boiling and keep boiling for several minutes. This is necessary to get the antimony sulfate completely into solution, as it crystallizes out from a cold concentrated sulfuric acid solution. Allow the lead sulfate to settle out for about five minutes or until the solution is clear, but do not allow the temperature of the liquid to fall below about 60° C. The liquid above the PbSO₄ should become clear quickly. If it does not, it should be heated longer. After the liquid has become clear, pour it through a weighed Gooch crucible with an asbestos mat. Pour the solution off as completely as possible without allowing more than a very small amount of the PbSO₄ to go over into the crucible.

Now introduce 10 cc. more of concentrated sulfuric acid into the Kjeldahl and heat to boiling and keep boiling several minutes, cool, add 30 cc. of water, heat to boiling for a few minutes, allow the solution to cool to about 50° C. and pour it and the precipitate of lead sulfate into the Gooch crucible. Wash the crucible and precipitate six or eight times with distilled water, taking care to keep the volume of the filtrate down to 125–150 cc. Ignite the PbSO₄ at a dull red heat, preferably in a muffle furnace, for fifteen minutes or more, cool and weigh. It contains 68.3 per cent lead.

Pour the filtrate from the PbSO₄ into a 450 cc. Erlenmeyer flask, heat to 60°–80° C. and titrate the antimony with standard permanganate of about

N/10 strength. After some permanganate has been run in, the solution takes on a pink tinge but the addition of the permanganate is continued until the color becomes a deep permanganate; then two or three cc. more of permanganate are added. Stir the solution for a minute then titrate the excess permanganate with a standard ferrous sulfate solution until the pink just disappears. This is the end point and it is quite sharp.

The permanganate should be standardized by dissolving 0.2 gram of pure antimony in 30 cc. of boiling concentrated sulfuric acid and, after diluting to 150 cc., titrating with permanganate at 70° C. Fairly close results may be obtained by calculating the antimony strength of permanganate from its iron value by multiplying the iron value by 1.076, but it is much better to standardize against pure antimony.

After the antimony is titrated, the tin is determined according to the method of Low improved by Patrick and Wilsnack.¹ Add to the solution 50 cc. of hydrochloric acid and about 0.15 gram of antimony dissolved in 5 cc. of concentrated sulfuric acid unless there is already that amount of antimony present, in which case no antimony need be added. Insert into the neck of the flask a three-hole rubber stopper. Through one hole pass a glass tube which reaches to the bottom of the flask. Between the stopper and the flask and opposite the other holes, pass a platinum wire on the end of which is a sheet of pure iron (such as ingot iron) about two inches long and one-half inch wide, which rests on the bottom of the flask. Pass CO₂ or hydrogen or natural gas (which has bubbled through NaOH solution to remove H₂S) through the glass tube, and heat the solution to slow boiling; continue the boiling and the stream of gas for thirty minutes after the solution has become colorless. The antimony precipitates out and with the iron reduces the tin to the divalent condition. Cool the solution while a rapid stream of the gas is kept passing through the flask to keep out air. When cold add through a funnel in one of the holes in the stopper 100 cc. of cold, recently boiled, distilled water containing several cc. of starch solution. Pull the iron sheet up out of the solution by means of the platinum wire. Remove the funnel and while a slow current of gas is passing, insert the tip of a burette through one of the holes and titrate the tin with a *N/10* iodine solution until a blue color is obtained. The end point is very sharp but will fade after several minutes. The results are quite accurate.

At the same time that the above sample is being analyzed, another sample should be similarly treated up to or *through* the antimony titration, if the chemist desires duplicate results on the lead and antimony. To the sulfuric acid solution add three grams of tartaric acid, next ammonia until the solution is slightly alkaline, and then two cc. of sulfuric acid; heat nearly to boiling. Add two grams of sodium sulfite and when it is all dissolved add a gram of KCNS dissolved in 10 cc. of water. Shake the flask well and allow the CuCNS to settle for fifteen minutes while the solution

is kept hot. Filter through an asbestos mat, wash well with water, and determine the copper in the precipitate by either the sulfocyanate-permanganate method or by the iodide method after igniting the precipitate and dissolving the copper oxide in nitric acid.

NOTES ON THE PROCESS

1. When an alloy containing lead or tin is dissolved in hot sulfuric acid, there is considerable free sulfur liberated. This does no harm.

2. The alloy must be digested with the sulfuric acid at a boiling heat for several minutes in order to dissolve it completely and to oxidize all the tin to the "ic" form. There is no tendency for the antimony to be oxidized further than to the trivalent state.

3. It is necessary that the lead sulfate be ignited at a dull red heat for some time since it seems to hold excess sulfuric acid very tenaciously. Even then the results tend to run a little high.

4. In the antimony titration it is necessary to employ a large excess of permanganate in order to complete the oxidation. Often the solution will become turbid during the titration, but this does not affect the results. When the titration is made thus, in a solution free from HCl, the end point is not evanescent.

The following are some results obtained by the above method:

Grams Lead		Grams Antimony		Grams Tin		Grams Copper	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
0.600	0.602	0.200	0.200	0.200	0.201	0.0460	0.0450
0.600	0.599	0.200	0.201	0.200	0.201	0.0440	0.0440
0.600	0.602	0.200	0.199	0.1350	0.1340
1.000	1.001	0.200	0.200	0.200	0.200	0.0430	0.0425
0.500	0.502	0.250	0.250	0.250	0.252	0.0890	0.0894
...	...	0.200	0.200	0.200	0.917	0.0500	0.0500
0.700	0.703	0.300	0.301	0.150	0.149	0.2500	0.2510
0.500	0.500	0.250	0.249	0.250	0.250	0.0500	0.0500
0.700	0.701	0.150	0.148	0.0500	0.0490
0.600	0.601	0.200	0.200	0.200	0.200	0.0255	0.0250
0.600	0.600	0.200	0.200	0.200	0.200	0.0255	0.0254
...	0.0255	0.0240
...	0.0255	0.0256

The copper in the above experiments was determined by the sulfocyanate-permanganate method.¹

The purity of the metals used was ascertained by determining the most likely impurities in them. The weights taken in the above experiments were such as to give the amounts recorded.

DEPARTMENT OF METALLURGY
OHIO STATE UNIVERSITY
COLUMBUS

A RAPID AND ACCURATE GRAVIMETRIC METHOD FOR DETERMINING FAT IN ICE CREAMS, CEREALS AND CHOCOLATE

By E. P. HARDING AND GUY PARKIN

Received July 14, 1913

In THIS JOURNAL, 5, 131, the authors of this paper described a method for determining milk-fat in evaporated milk and milk powders at the conclusion of which they stated that the method was at that time being tried out on various ice creams, on cheese, cereals, flours and various other products.

The present paper is a continuation of that work

¹ THIS JOURNAL, 4, 597.

¹ THIS JOURNAL, 5, 215.