

during slacking. It was found that slacking could be prevented in large degree by storing in tight covered bins, but that in both open and closed bins, with slacking and without, the coal lost in eight months about 5 per cent. of its heat value.

The laboratory investigation has shown that coal absorbs oxygen most rapidly immediately after mining. The sample from Saline Co., Illinois, for example, absorbed 2 liters or more of oxygen in the first four days after mining, and after five months the rate of absorption had decreased to approximately 0.7 liter in four days. This rapid absorption of oxygen just after mining suggests the advisability in order to avoid spontaneous combustion, of keeping fresh coal more or less open and cooled by ventilation until a proper time has elapsed after mining. Experiments are now being begun in the laboratory to show the comparative rise in temperature and absorption of oxygen by different coals on passing air through a sample a given length of time at 100° C. The effect also of fineness of division and amount of surface exposed on the absorption of oxygen is likely to be large and will be investigated.

To summarize the results of the investigation thus far accomplished, coal absorbs oxygen from the air during storage without forming CO₂ and the amount of oxygen absorbed accords approximately with the deterioration in heat value. Oxidation may be largely prevented by immersion under water. Methane is evolved from freshly mined coal in quantities of importance as bearing on mine explosions but of no importance as a loss of fuel value. Outdoor tests are being conducted to determine the extent of the loss during storage in the open as compared with immersion under water. Laboratory by-product tests are being carried on to determine changes in the yields of gas, tar and ammonia through deterioration in storage.

THE ANALYSIS OF BABBITT METALS; SOLDERS AND JOURNAL BRASSES.

By D. J. DEMOREST.

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The separations involved in the analysis of these alloys of lead, copper, antimony, and tin as ordinarily carried out are long and tiresome. Furthermore, the results obtained are not always satisfactory.

In the analysis of alloys containing tin with lead and copper, but no antimony, the usual procedure is to separate the tin from the other metals as metastannic acid by means of nitric acid. This metastannic acid, however, is always contaminated with oxides of lead and copper and phosphorus, which cannot be washed out. The old method of removing these oxides is to fuse the SnO₂ with sodium carbonate and sulphur and to dissolve out the sulphostannate formed, leaving the lead and copper as sul-

phides. Sometimes two fusions are required. This method is time-consuming and troublesome.

Experiments by the writer show that accurate results can be obtained in a short time by the following procedure: The metastannic acid is dissolved in NH₄HS, leaving the lead and copper as insoluble sulphides. This NH₄HS solution is electrolyzed, giving very accurately and quickly the amount of tin in the sample. The sulphides of lead and copper are added to the main solution of lead and copper, which is then electrolyzed.

This NH₄HS treatment of the metastannic acid with subsequent electrolysis is new, so far as the author is aware.

When antimony is present, as well as tin (as in type metals and babbitts), the nitric acid separation, as above mentioned, cannot be used because antimony is not rendered entirely insoluble by the acid. The old method of separation by means of alkaline sulphides has to be used. But this process, as given in various texts, consumes much time and, according to the author's experience, is very liable to leave some antimony and tin with the lead and copper. The results of many experiments, however, show that this method can be modified so as to give complete separation in 3/4 of an hour after the sample is weighed up, instead of two to four hours, as required by the ordinary way. The modification involves the solution of the sulphides of lead and tin in nitric acid and then precipitation of the lead and copper a second time as sulphides.

After the antimony and tin have been separated from the lead and copper, the standard method has been that of Clark¹ for the separation of antimony from tin. In this method the antimony is separated from the tin by precipitation by H₂S in oxalic acid solution and the sulphides weighed up. Also the method of Rose, modified by Hampe,² in which the antimony is precipitated as sodium antimoniate. But these methods are also long.

The results of experiments show that from an NH₄HS solution antimony and tin can be quickly and quantitatively precipitated together in a pure state electrolytically.

Further, it was found that the deposit can be dissolved from the electrode without loss, the antimony oxidized to H₃SbO₄ and titrated accurately iodimetrically. The tin is obtained by difference. This precipitation of antimony and tin together, electrolytically, with subsequent titration of the antimony, is new so far as the author is aware.

The writer tried to use the method of electrolyzing the antimony and tin solution in a Na₂S solution, from which the antimony only is supposed to separate, but the process did not prove successful.

¹ Chem. News, 21, 124.

² Chem. Ztg., 18, 1900.

The whole process for the determination of lead, copper, antimony and tin can be completed easily in $3\frac{1}{2}$ to 4 hours.

During the first part of this investigation, the writer used rotating anodes or cathodes in the electrolysis with good results. But there is some trouble in keeping good electrical connections with the rotating electrode unless an expensive mercury cup contact is used and in almost all the work on alloys containing both antimony and tin, stationary electrodes were used, one of which is a platinum gauze cylinder, 2" high and 1" in diameter, upon which the metals were precipitated. To hasten the precipitation the solution was agitated by means of a platinum paddle operated by a water motor. The deposits are all very adherent and dense. The motor was belted to a group of six stirrers, so that many different depositions can be carried on at once. Using a gauze cathode and rotating the solution in this way it is possible to deposit 0.300 gram of copper quantitatively in 10 to 15 minutes. A particular advantage of rotating the solution instead of the anode or cathode is that it permits the use of any style of electrode.

The methods in detail are as follows:

I. ANTIMONY NOT PRESENT (AS IN SOLDER AND JOURNAL BRASSES).

Two grams of the journal brass are dissolved in nitric acid (sp. gr. 1.42) and evaporated to dryness to bring the metastannic acid to such a condition that it will not clog up a filter paper. The use of a gentle air blast over the solution facilitates the evaporation. To the residue 50 cc. of water and 5 cc. of HNO_3 are added, heated to dissolve the lead and copper, etc., and filtered. The metastannic acid on the filter is washed two or three times and then washed back into the beaker or flask in which the metal was dissolved. 25 cc. of NH_4HS (made by saturating NH_4OH , (sp. gr. 0.9) with H_2S) are poured through the filter and into the flask. This will dissolve all the metastannic acid and precipitate as sulphides the lead and copper which contaminated the tin. The flask and its contents are heated and shaken for about ten minutes and then the solution poured through the same filter as before, catching the NH_4HS solution of the tin in a 300 cc. beaker. The sulphides on the filter are washed with water containing some NH_4HS . The filtrate is diluted to 200 cc. The small amount of PbS and Cu_2S is dissolved in a little nitric acid and added to the main solution of lead and copper.

One hundred cc. of the tin solution are pipetted off, 10 cc. of NH_4HS and 4 grams KCN are added and the solution electrolyzed with a 5- to 6-ampere current, rotating the solution as described below under the analysis of alloys containing both antimony and tin.

The solution of lead and copper is diluted to 200

cc., 50 to 100 cc. (according to the amount of lead present) are pipetted off, 15 cc. HNO_3 added, and the solution is electrolyzed, using a 5- to 6-ampere current and rotating electrode as described below.

Any iron and zinc in the metal are left in the solution from which the lead and copper are deposited. If it is desired to determine these, the solution is evaporated to dryness, dissolved in a little HCl , the iron oxidized with H_2O_2 and precipitated with ammonia. The filtrate from the iron is made strongly acid with HCl and boiled to decompose the H_2O_2 . The solution is then titrated with $\text{K}_4\text{Fe}(\text{CN})_6$, using uranium acetate indicator.

The following are some results obtained by this method upon two samples of journal brasses:

	Wt. of Cu.	Wt. of Pb.	Wt. of Tin.
No. 1.....	0.7592	0.1304	0.0701
	0.7590	0.1305	0.0705
	0.7592	0.1300	0.0703
No. 2.....	0.7856	0.1012	0.0909
	0.7866	0.1006	0.0905
	0.7842	0.1010	0.0905
	0.7844	0.1002	

2. ANTIMONY PRESENT, (AS IN BEARING METALS).

One gram of the alloy is placed in a 200 cc. beaker and covered with 20 cc. of water. In this are dissolved 5 grams of tartaric acid and then 10 cc. HNO_3 (sp. gr. 1.42) are added. This will dissolve the alloy quickly unless it is in large pieces, which it never need be. When dissolved the solution is diluted to 50 cc. and a strong solution of NaOH is poured in until the hydroxides first formed dissolve and leave the solution clear. The liquid should not be heated as this may cause a precipitate of metastannic acid to commence to form in the alkaline solution. The solution is poured slowly and with constant shaking into a flask containing 150 cc. of a boiling hot solution of 10 grams of NaOH and 10 cc. of a colorless saturated solution of Na_2S . (The solution should be colorless or some copper will remain in the solution.) The contents of the flask are agitated for several minutes and then allowed to settle. The sulphides of lead and copper will settle quickly and compactly. The clear solution is decanted as closely as possible through a strong filter paper folded in ribs. The precipitate is washed twice by decantation, using about 25 cc. of water each time.

Now to the sulphides in the flask 5 cc. of HNO_3 are added and heated until the black sulphides disappear. Then the solution is made alkaline with NaOH again and 10 cc. Na_2S solution added and heated and shaken vigorously for several minutes. Again the supernatant liquid is decanted through the same filter, washed twice by decantation and then the sulphides transferred to the filter and washed twice more with hot water containing a little Na_2S .

The filter paper with its contents is placed in a crucible and heated gently so as to dry the sulphides.

While these are drying, sulphuric acid is added un-

der a hood to the filtrate which contains the Sb and Sn until the solution, which should have a volume of 400 to 500 cc., is acid. The liquid is stirred well and allowed to settle for a few minutes, then decanted through a filter paper as closely as possible to get rid of the greater part of the liquid. The beaker containing the sulphides of antimony and tin is set under the funnel, and 25 cc. of the NH_4HS solution diluted to 50 cc. are poured through. This will dissolve the sulphides. The solution is transferred to a 300 cc. beaker, diluted to 150 cc., 4 to 5 grams KCN are added, and the solution electrolyzed, the solution being rapidly rotated.

The cathode used was a cylinder of platinum gauze, 2" high and 1" in diameter. The voltage used was 8 to 10 volts and the current 5 to 6 amperes. This large current will heat the solution considerably and it is best to set the beaker in a basin of water. The KCN keeps sulphur from separating out on the anode in excess by forming KCNS with the polysulphides.

The tin and antimony should be deposited in 30 to 60 minutes, depending on the amounts present. The cathode is lifted out and washed first with water, then with alcohol, and dried on a steam plate. If any pieces of sulphur are entangled in the meshes of the gauze, dip the cathode in CS_2 before washing with alcohol. This, however, is rarely necessary.

After weighing, the solution is again electrolyzed for ten minutes and the cathode washed and weighed. If the weight has not increased more than 1 mm. in these ten minutes the electrolysis is complete.

After the cathode is weighed it is placed in a small beaker and 5 cc. of strong HNO_3 are poured over it from a pipette. The acid is heated and the beaker tipped and the electrode turned so that the HNO_3 will dissolve off all the deposit that is possible. There will always be some black stains left on the cathode, which are very difficult to remove with HNO_3 . The gauze is washed with a fine jet of water over the beaker. Then the gauze is set into another small beaker and 60 cc. of a strong HCl are poured over it, which will dissolve off the black stains. The HNO_3 is used first to avoid the loss of antimony as SbH_3 , which would take place if the deposit were dissolved in HCl alone.

The gauze is then washed with a jet of water into the HCl and the two solutions poured into a 500 cc. Erlenmeyer flask and the beakers washed with a little more HCl. The solution should be boiled vigorously for 10 to 15 minutes to decompose the HNO_3 .

Or, instead of mixing the two solutions, the 5 cc. of HNO_3 are evaporated to dryness in a platinum dish (for speed), then the residue is dissolved in 60 cc. HCl. This last way is the best but takes more time.

Now, to the hot HCl solution 5 grams of KClO_3 are added in small amounts at a time, then 50 cc.

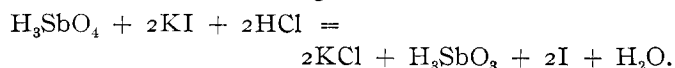
H_2O are poured in and the solution boiled while passing through a stream of CO_2 until the free chlorine is all gone, as shown by starch-iodide paper. This takes 15 to 20 minutes.

The KClO_3 must not be added before the HNO_3 is decomposed, for the KNO_3 formed greatly prolongs the time necessary to get rid of all free Cl.

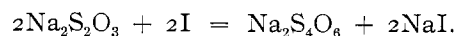
When the free chlorine is all gone water is added to make a volume of 150 cc. and the solution cooled under tap water while passing in a stream of CO_2 to displace the air. The solution should be colorless. The CO_2 is made from marble and HCl.

When cool, the current of CO_2 is stopped, 4 grams KI are added and the liquid stirred until the KI is all dissolved. Then standard $\text{Na}_2\text{S}_2\text{O}_3$ solution is run in until the color due to iodine all disappears, starch solution is added, and the excess thio titrated back with standard $\text{K}_2\text{Cr}_2\text{O}_7$ until a blue color is obtained. This should take only a few drops. The writer prefers this end point to merely titrating with $\text{Na}_2\text{S}_2\text{O}_3$ until the blue starch iodide disappears.

The KClO_3 oxidizes the antimony to H_3SbO_4 . This liberates iodine according to the reaction:



Then the thiosulphate is oxidized by the iodine in the reaction:



The writer standardizes the thiosulphate against $\text{K}_2\text{Cr}_2\text{O}_7$ of known iron strength. Also by treating Sb_2O_3 or Sb or tartar emetic by dissolving them in HCl and KClO_3 and treating as above. The two methods of standardization check very closely. The iron strength of the bichromate, multiplied by 1.0751, gives its antimony value. The "thio" solution is made by dissolving 20.7 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and diluting to one liter. The author does not like the use of SnCl_2 for the titration as it changes strength so rapidly.

There is nothing which can be deposited with the antimony and tin which will interfere with the process. Arsenic does not interfere.

While the electrolysis of the antimony and tin is going on, the dried sulphides of lead and copper are crumbled into a beaker, the paper burned and the ash added to the rest in the beaker. The sulphides and ash are dissolved in 40 cc. concentrated HNO_3 . In this solution the lead may be determined as sulphate and the copper in the filtrate from the lead titrated by the iodide method. But it is much quicker and more accurate to determine the two electrolytically, according to the following:

The solution is diluted to 100 cc., 50 cc. are pipetted into a platinum dish, 50 cc. of water added and electrolyzed with a potential of six volts for a few minutes. The voltage is then increased to 10 to 12 volts,

keeping the solution stirred. The lead is all deposited on the dish, which is the anode, in about 15 minutes. Then part of the HNO_3 is neutralized with ammonia and the electrolysis continued for 15 minutes, when the copper is all deposited on the gauze cathode. The electrodes are washed quickly with water, then with alcohol, dried and weighed. The PbO_2 should be dried at above 200°C . to expel water.

To show that antimony and tin are deposited quantitatively the following results are given:

Present.				Found.			
Lead.	Copper.	Antimony.	Tin.	Sb+Sn.	Antimony.	Tin.	Cu.
0.700	0	0.1500	0.1000	0.2515	0.1480	0.1035	...
0.700	0	0.1000	0.2495	0.1495	0.1000	...
0.700	0.0500	0.1500	0.1000	0.2503	0.1490	0.1013	...
0.700	0.0500	0.1500	0.1000	0.2500
0.700	0.0500	0.1500	0.1000	0.2480	0.1480	0.1000	0.050
...	0.1800	0.1800
...	0.1500	0.1500	0.3005	0.1505	0.1500	...
...	0.1500	0.1000	0.2495	0.1490	0.1005	...
...	0.1500	0.1000	0.2515	0.1495	0.1020	...

Present.				Found.			
Lead.	Copper.	Antimony.	Tin.	Lead.	Copper.	Sb+Sn.	Sb. Sn.
0.6500	0.050	0.1500	0.1500	0.6505	0.05050	0.2999	0.1496 0.1503

In this last analysis the thiosulphate was standardized against $\text{K}_2\text{Cr}_2\text{O}_7$ solution, giving as the strength of the thio 1 cc. = 0.00504 gram antimony. Then 0.200 gram of pure Sb_2O_3 was dissolved in HCl and KClO_3 and treated as in the regular process. Result, 1 cc. = 0.00504 gram Sb. This was then repeated except that 5 cc. of HNO_3 were used as in the process. Result, 1 cc. = 0.00504 gram Sb.

The electric current used in the work at the Department of Metallurgy was obtained from an alternating current 110-volt lighting circuit rectified by means of a chemical transformer, designed by the writer, making use of the well-known aluminium method. The rectifier was able to transform 10 amperes for 60 hours without trouble and has been in use for a year without any repairs. The aluminium and lead electrode were each $3\frac{1}{2}$ " by 10" by $\frac{3}{8}$ " and were immersed in a saturated solution of $(\text{NH}_4)_3\text{PO}_4$ in glass cylinders around which water circulated. Four cells were used and connected as described in Perkin's "Practical Methods of Electro-Chemistry." 85 per cent. of the a. c. was rectified.

Almost all the experimental work on alloys containing both antimony and tin upon which the foregoing processes were based was done at the laboratory of the Department of Metallurgy of the Ohio State University. The rest was chiefly done at the laboratory of the Union Pacific Railroad at Omaha.

SUMMARY.

Antimony and tin may be separated from lead and copper by the alkali sulphide method in three-quarters of an hour.

Metastannic acid may be purified by dissolving it in NH_4HS and filtering off the sulphides of copper

and lead. This NH_4HS can then be electrolyzed for tin.

Antimony and tin may be accurately and quickly deposited together electrolytically from a solution of their sulphides dissolved in NH_4HS .

The deposit of antimony and tin may be dissolved off the electrode and the antimony oxidized, to H_3SbO_4 and titrated accurately.

Rapid electrolysis with excellently adhering deposits may be accomplished when gauze electrodes and mechanical stirring of the solution are used.

Alloys of lead, copper, antimony and tin may be accurately analyzed in three to four hours.

DEPARTMENT OF METALLURGY,
OHIO STATE UNIVERSITY,
Jan. 12, 1910.

[CONTRIBUTION FROM ARTHUR D. LITTLE, INC., LABORATORY OF ENGINEERING CHEMISTRY.]

THE LIBRARY AS AN ADJUNCT TO INDUSTRIAL LABORATORIES.

By GUY E. MARION.

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It has been recently said:¹ "The financial library of the present day is a comparatively recent institution, and many causes have contributed to its development." Equally true is this statement in its application to the library as an adjunct to industrial laboratories. Let us review for a moment, then, the causes which have contributed to the usefulness and development of the Laboratory Library. Many of them are the same as those which are causing to spring into existence the increasing number of small specialized libraries about the country in general. The chief cause, however, is the phenomenal growth of all business, which continually necessitates the introduction of new methods for expediting its procedure. Specialization has entered here as elsewhere, and it has been found better to have one man prepared to answer the many inquiries of a general nature coming to the laboratory than to be forced to distribute these inquiries throughout the staff. This has meant, then, the collecting of the laboratory's resources (books, pamphlets, experimental data, catalogues, documentary experience, etc.) at one point into a library. In this way a new channel has been formed for the transaction of a portion of the laboratory's business, namely, the answering of the general inquiries arising both in and outside its ranks; and the library has become a vital factor in the operation of the organization. But, not only has the work been better systematized by the advent of the library; its coming has enabled the laboratory to accept wider opportunities, to enter with less hesitation new and unexploited fields, and to increase its efficiency in a large number of ways which make for confidence

¹ From a paper entitled "Some Aspects of a Financial Library," by Beatrice E. Carr, presented at the first annual meeting of the Special Libraries Association.