Tuble I'l Debe mutha muterial for standard darie	Table IV.	Best Matrix Material for Standard Curve	
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(Maximum deviation factor of impurity element from true amount does not exceed 2)						
$\mathbf{Element}$	Range, P.P.M.	MgO	С	NaCl	РЬО	Fe
Be	100-1000		*	*	*	
Sh	5000-50.000	*	*	*	*	*
ĩ	2000-50.000		*	*	*	
Ċd	5000-50,000	*	*	*		
Mn	200-50.000		*			*
Sn	1000-50,000	*		*		
Co	5000~50,000			*		

by the proper choice of matrix for the standard curve, to a high factor of 2 and a low factor of 0.5.

The presence of a large number of impurities or a large quantity of any one element does not affect these limiting factors.

ACKNOWLEDGMENT

Acknowledgment is made to Norman H. Nachtrieb for the initiation of the problem and guidance in the interpretation of the data.

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Photometric Determination of Sulfur in Metals and Alloys

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A photometric method for the determination of sulfur in metals and alloys is described. The method consists of solution of the sample in a mixture of hydrochloric and nitric acids, destruction of the nitric acid, reduction of the sulfate to sulfide with the aid of hydriodic acid, distillation of the hydrogen sulfide into a solution of ammonium hydroxide, and finally precipitation as colloidal lead sulfide and measurement of the transmittancy of the sulfide sol at 370 m μ .

METHOD published by the author a few years ago (2-4) has $\mathbb A$ been used extensively in these laboratories for the determination of sulfur in metals and alloys. It consists of solution of the alloy in a mixture of nitric and hydrochloric acids, destruction of the nitric acid, reduction of the sulfate to sulfide with the aid of hydriodic acid and distillation, and iodometric titration of the resultant hydrogen sulfide. In order to increase the sensitivity of this method it has been modified to provide for a photometric determination of the sulfur as lead sulfide-a procedure suggested by the work of Field and Oldach (1). Suitable techniques have been developed to make it applicable to the determination of 1 to 50 micrograms of sulfur in 0.1 to 1 gram of most of the common metals and alloys.

APPARATUS

Distillation Apparatus. The distillation apparatus diagramed in Figure 1 was used.

Photoelectric Photometer. An Evelyn photometer was used in the present investigation and the procedure was written with this instrument in mind, but any instrument of comparative quality is suitable.

REAGENTS

Standard Potassium Sulfate Solution (1 ml. = 5 micrograms of sulfur). Transfer 27.2 mg. of pure dry potassium sulfate to a 1-liter volumetric flask, dissolve, and dilute to the mark with distilled water

Redistilled Hydrochloric Acid. Transfer 500 ml. of hydrochloric acid (specific gravity 1.19) and 450 ml. of distilled water to a 1500-ml. standard-taper round-bottomed Pyrex flask and add a few grains of 12-mesh silicon carbide. Connect to an allglass water cooled distillation apparatus and heat to boiling. When enough of the acid has been distilled over to wash out the condenser system and to ensure that the acid coming over is constant boiling—e.g., 50 ml.—replace the receiver with a clean Pyrex bottle. Continue the distillation until the volume in the flask has been reduced to 100 ml. Stopper and reserve the distilled acid.

Redistilled Nitric Acid. Distill undiluted nitric acid (specific gravity 1.42) in the manner described above into a clean Pyrex bottle, discarding the first 25-ml. portion of acid that comes over. Stopper and reserve.

Redistilled Formic Acid. Oxidize the sulfite in commercial formic acid by titration with 0.1 N potassium permanganate

 until the solution acquires a pink tint which persists for a few seconds. Distill as directed above. Stopper and reserve.
 Hydriodic Acid-Hypophosphorous Acid Mixture. Transfer 100 ml. of hydriodic acid (specific gravity 1.70) and 25 ml. of hypophosphorous acid (50%) to a clean 250-ml. Vycor Erlenmeyer flask. Add a few grains of clean 12-mesh silicon carbide, heat to vigorous holling without a cover on a hot clearing bet. heat to vigorous boiling without a cover on a hot electric plate, and boil for exactly 3 minutes. Cover and cool to room temperature. Ignore any iodine that may appear in the solution on standing.

Lead Citrate Solution. Dissolve 5 grams of lead nitrate in 50 ml. of distilled water and dilute to 100 ml. Add 20 grams of citric acid and warm to dissolve. If a precipitate appears on standing, use only the supernatant solution or allow to stand overnight and then decant from the precipitate.

PROCEDURE

Preparation of Calibration Curve. Add from a buret 0, 2, 4, 5. So and 10 ml. of the standard potassium sulfate solution (1 ml. = 5 micrograms of sulfur) to clean 50-ml. standard-taper Pyrex Erlenmeyer flasks (Figure 1). (Take care to prevent contamination of the samples with sulfate from unclean glassware or impure chemicals. Whenever an acid or acid mixture is called for, use the redistilled acids described under reaconts). Conversely, and the same set of the same set. The same set of the sa use the redistilled acids described under reagents.) Carry each sample separately through the steps indicated below.

Evaporate nearly to dryness on a hot plate, in an oven or even over a flame, providing the flaming is done in a hood and the flask is held in such a position that any sulfur acids from the

flame do not enter the flask. Cool to room temperature and add 5 ml. of hydrochloric acid. Add 15 ml. of hydriodic-hypophosphorous acid mixture, making sure that a drop or two falls on the ground-glass joint, so that the latter will be wet in the subsequent distillation. Stopper at once with the distillation head and immediately dip the arm into 15 ml. of ammonium hydroxide (1 to 2) in a clean 25-ml. volumetric flask. [It is imperative that the volumetric flask and the side arm of the distillation head be freed of any lead salts (that may be present from a previous analysis) by washing in nitric acid (1 to 1) and then distilled water.]



Figure 1. Distillation Apparatus

Place the Erlenmeyer flask on a definite spot on a hot plate, so that the center of the flask is 5 cm. in from the edge of the plate. Arrange to surround the volumetric flask with a crushed ice bath as indicated in Figure 1. The surface temperature of the hot plate should be previously adjusted with a Variac, so that a thermometer will read $185^{\circ} \pm 3^{\circ}$ C. when its bulb is suspended near the bottom of a 30-ml. beaker (containing 15 ml. of Dow Corning 550 silicone oil) placed next to the spot on the plate reserved for the 50-ml. Erlenmeyer flask. (The temperature chosen for the distillation is not critical, providing that it is somewhere in the region of 185° C. and is maintained constant.) Connect the distillation head immediately to a tank of pure nitrogen (previously adjusted to a definite rate of flow), using a

Connect the distillation head immediately to a tank of pure nitrogen (previously adjusted to a definite rate of flow), using a rubber tubing that is not likely to give off any sulfur or sulfur compounds to the nitrogen that passes through it. (To prevent oxidation of the sulfide it is essential that the sample be at room temperature and that the nitrogen line be connected immediately, in order that removal of air from the flasks will be completed before distillation of the sulfide begins.) The rate of flow of nitrogen must be rather closely controlled if reproducible results are to be obtained. To do this it is recommended that the flow be regulated by means of the usual pressure gage until the rate is such that 100 ml. of water are displaced in 30 ± 1 seconds from an inverted water-filled 100-ml. graduate when the end of the rubber hose is held under the graduate as the latter is suspended to a denth of 2.5 cm. in a water bath.

to a depth of 2.5 cm. in a water bath. Distill for exactly 5 minutes after the first appearance of white fumes escaping from the volumetric flask, keeping the latter in intimate contact with crushed iced by removal of excess water and replacement with ice. (Sulfide will be lost if the ammonium hydroxide solution is not kept cold. Even with this precaution the amount of sulfide that can be safely held is limited.) Finally

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remove and separate the flasks. Immediately pipet 1 ml. of the lead citrate solution to the volumetric flask, swirl, dilute to the mark, mix well, and transfer to a dry absorption cell. Read the per cent transmittancy at 370 mµ with the instrument set at 100% transmittancy with distilled water. (It is essential that all operations from the finish of the distillation to the reading of the per cent transmittancy be done as quickly as is convenient, in order to prevent oxidation of the ammonium sulfide and to obtain the photometric reading before appreciable agglomeration of the colloidal lead sulfide takes place.) Prepare a standard curve by plotting, on semilog paper, micro-

Prepare a standard curve by plotting, on semilog paper, micrograms of sulfur against per cent transmittancy values that have been corrected for the blank. The latter should correspond to not more than about 0.5 microgram of sulfur. The corrected per cent transmittancy values are obtained as follows:

 $\frac{\% T \text{ of sample } vs. \text{ H}_2\text{O}}{\% T \text{ of blank } vs. \text{ H}_2\text{O}} \times 100 = \text{corrected } \% T$

Analysis of Sample. Transfer 0.1 to 1 gram of the sample, depending on the sulfur content, to a clean 50-ml. standardtaper Pyrex Erlenmeyer flask (Figure 1). (For samples that dissolve with unusual violence—tin, aluminum, and magnesium alloys—the initial solution is best accomplished in a clean covered 150-ml. beaker.) For a 1-gram sample add 10 ml. of a freshly mixed solution of 80 ml. of hydrochloric acid and 20 ml. of nitric acid. (If a sample smaller than 1 gram was taken in order to keep the amount of sulfur to be determined below 50 micrograms, it will be necessary to reduce proportionately the amount of solvent acids used, or boil off the excess after solution of the sample, in order to avoid using too much formic acid.) Cover and heat gently to start dissolution of the sample. Cool in an ice bath if the initial reaction becomes too violent. Continue to heat gently until solution of the sample is complete. (If hydrolysis occurs at any time up to the point where complete destruction of the nitrates has been accomplished, add 5 ml. of hydrochloric acid.)

Place the flask on a hot plate with surface temperature of about 130° C. and add from a medicine dropper about 0.5 ml. of formic acid. Cool the flask in an ice bath if the reaction becomes too violent. Continue the addition of small portions of formic acid until gas ceases to be evolved from the solution and it is evident that nitrogen acids have been completely destroyed. In general, not more than 1 or 2 ml. of formic acid will be required. Boil down as far as possible—to 1- or 2-ml, volume—on a flame to expel formic acid. Add 10 ml. of hydrochloric acid and boil down to 5 ml. on a flame. Cool to room temperature.

In general, not more than 1 or 2 mit, of formic acid will be required. Boil down as far as possible—to 1-or 2-ml. volume—on a fame to expel formic acid. Add 10 ml. of hydrochloric acid and boil down to 5 ml. on a flame. Cool to room temperature. Add 15 ml. of hydriodic-hypophosphorous acid mixture, cap with the distillation head, and dip the arm into 15 ml. of ammonium hydroxide (1 to 2) in a clean 25-ml. volumetric flask as directed above. (For copper and copper alloys it is best to use 20 ml. of the hydriodic-hypophosphorous acid mixture to ensure complete solution of the cuprous iodide and thus to prevent bumping.) If heat is generated on adding the acid mixture or if iodine is liberated in the solution in the distilling flask, cool to room temperature, allow to stand, and shake occasionally until the iodine has been reduced. Finally place the flask on the hot plate, connected to the nitrogen, and proceed with the distillation and photometric determination as directed above. Run a blank through the entire procedure, using equivalent quantities of acids and taking precautions not to lose sulfuric acid during the evaporations. The blank should correspond to not more than about 1 microgram of sulfur. (The destruction of the nitric acid with formic acid is more difficult to initiate when running a blank than it is for a sample. This suggests that the reduction reaction is catalyzed by certain metal ions.) Obtain the corrected per cent transmittancy for the sample and read from the standard curve the weight of sulfur present in the sample.

PRECAUTIONS AND MODIFICATIONS OF PROCEDURE REQUIRED IN ANALYSIS OF CERTAIN METALS

Arsenic, Antimony, Tin, and Germanium. Arsenic precipitates first as the iodide and then as metal during the sulfide distillation. For this reason it is best to limit the sample size to 0.5 gram to minimize bumping. If a larger sample is to be analyzed it may be best to resort to removal of the arsenic by distillation as bromide, using the method described below for selenium.

When analyzing antimony it is necessary to add an extra 5 ml. of hydrochloric acid with the 10 ml. of hydrochloric-nitric acid mixture used for solution of the sample. This precaution plus that of keeping the flask covered during solution of the

sample will prevent hydrolysis of the antimony. The hydrolysis is harmful only in that it may prevent complete destruction of the nitrates in the solution.

Care must be taken in the solution of tin alloys to prevent loss of the sample due to the violent boiling that occurs as the divalent tin suddenly goes over to the oxidized state.

Germanium precipitates as the oxide on solution in the acid mixture. In order to reduce the bumping and to minimize the amount of germanium that accompanies the sulfide in the subsequent distillation, it is best to remove the bulk of the germanium by distillation as follows:

Dissolve 0.5 gram of the sample in 10 ml. of hydrochloric-nitric acid mixture in the usual manner. Remove the cover and boil down on a flame to about 0.5 ml. Repeat the distillation one or more times by adding 10 ml. of hydrochloric acid and boiling down to 0.5-ml. volume. Care must be taken to avoid loss of sulfuric acid. Finally add 10 ml. of hydrochloric acid, destroy the nitrates, and proceed with the distillation in the usual manner.

Some arsenic, tin, germanium, and probably antimony will accompany the sulfide in the distillation, but this usually causes no trouble. Evidence of the presence of these metals in the distillates comes from the fact that the absorbancy of the lead sulfide solutions increases rather than decreases on standing. It is necessary to have sufficient hypophosphorous acid present to ensure complete reduction of tin to the less volatile stannous state; otherwise marked contamination of the distillate will take place.

Tellurium and Selenium. Tellurium precipitates as the metal during the sulfide distillation. In order to minimize bumping it is best, therefore, to limit the sample size to 0.5 gram. Selenium metal cannot be analyzed as directed in the procedure, for although most of it precipitates as metallic selenium during the distillation, appreciable quantities accompany the sulfide and precipitate as lead selenide in the photometric analysis. In order to obtain correct results for sulfur it is necessary, therefore, to resort to removal of the selenium by distillation as bromide.

Dissolve 1 gram of selenium metal plus 0.25 gram of relatively sulfur-free zinc or zinc alloy—e.g., Bureau of Standards zinc base No. 94—in 10 ml. of the hydrochloric-nitric acid mixture in the usual manner. Boil off the excess acid on a flame until a precipitate begins to appear—i.e., reduce the solution to 1- or 2-mi. volume. Cool, add 10 ml. of redistilled hydrobromic acid (prepare the sulfur-free acid by distilling 1 liter of hydrobromic acid, specific gravity about 1.38, in an all-glass still discarding the first 50 ml. that comes over), and boil down on a flame to about 0.5ml. volume. (There is danger of loss of sulfuric acid during the expulsion of the selenium if the sample is flamed to dryness and if zinc or some other metal is not present.) Transfer the flask to the hot plate used in the distillation of the sulfide and allow the rest of the hydrobromic acid to boil off, flaming the rest to the other the available of the gradient of the sulfide and allow the rest of the flash to available to available of the grad sides and top of the flask to expedite the expulsion of the acid. When all or nearly all of the excess hydrobromic acid has been expelled, cool the flask, add 2 ml. of hydrobromic acid, and repeat the distillation process. After the second removal of excess hydrobromic acid on the plate, add 2 ml. of hydrochloricnitric acid mixture, boil down on a flame to 0.5-ml. volume, add 5 ml. of hydrochloric acid and 0.5 ml. of formic acid, boil down to 0.5 ml. on a flame, add 5 ml. of hydrochloric acid, cool, add 15 ml. of hydriodic-hypophosphorous acid mixture, and distill as usual. Run a reagent blank, adding the 0.25-gram portion of zinc or zinc alloy.

Lead Alloys. Because of the low solubility of lead chloride it is necessary, if solution in hydrochloric-nitric acid solution is desired, to obtain the sample in as great a state of subdivision as possible before solution of the alloy is attempted. Even so, it is not always possible nor indeed necessary to accomplish complete decomposition of lead alloys, for this will usually take place upon subsequent boiling with the distillation mixture. Decomposition is best accomplished by heating gently on an asbestos pad, keeping the flask covered to prevent loss of too much acid, and adding more hydrochloric acid if necessary. Because little or no oxidizing action occurs during solution of a lead alloy, more formic acid will be required than is the case in alloys of copper or tin.

Lead Metal. Metallic lead must be dissolved in nitric acid.

Dissolve 0.5 gram of the sample in a mixture of 4 ml. of distilled water and 1 ml. of nitric acid with gentle heating. When solution is complete, boil on a flame until the volume is reduced to 1 ml. or until salts begin to precipitate. Add 25 ml. of hydrochloric acid and heat to dissolve all the lead chloride. Treat with formic acid to destroy nitrates, and proceed in the recommended manner, adding 15 rather than 10 ml. of hydrochloric acid after the expulsion of the formic acid.

Silver and Silver Alloys. Silver alloys that can be decomposed in the recommended hydrochloric-nitric acid mixture can be analyzed as directed. If severe bumping is encountered it is best to remove the silver chloride before treatment with formic acid.

The following procedure is recommended for silver metal.

Dissolve 1 gram in a covered 100-ml. beaker in a mixture of 2 ml. of nitric acid and 6 ml. of water with gentle heating. Add 10 ml. of hydrochloric acid, stir, and warm gently to coagulate the precipitate. Allow to settle and tamp down the precipitate. Decant the solution into a 50-ml. standard-taper Erlenmeyer distilling flask and wash the precipitate twice by decantation, using 3-ml. portions of hydrochloric acid. Ignore traces of silver chloride that may precipitate on cooling. Boil the solution down to 15-ml. volume, add formic acid to destroy the nitric acid, and proceed with the analysis in the usual manner.

Mercury. In the analysis of metallic mercury dissolve a 1-gram portion in 5 ml. of nitric acid with gentle heating. Boil the solution down to 0.5 ml., add 10 ml. of hydrochloric acid followed by formic acid, and proceed in the usual manner.

Molybdenum. When molybdenum metal is analyzed by the unmodified method very low results are obtained. Thus, when a 1-gram sample is analyzed only about 15% of the sulfur is recovered. By reducing the sample size the percentage recovery can be greatly increased. When a 0.5-gram sample is taken the recovery is about 85% and for a 0.25-gram sample it is about 95%. The low results may be due to depletion of reducing power of hydriodic-hypophosphorous acid solution due to the large valence change that occurs in the reduction of the molybdenum during the distillation, but further work needs to be done to prove this. [Almost complete recovery of the sulfur can be obtained in the analysis of 1 gram of chromium (present as ammonium vanadate)].

In view of the low results mentioned it is desirable, when analyzing samples containing over about 0.1 gram of molybdenum, to remove most of the latter by an ether extraction before performing the sulfur distillation.

Dissolve 0.5 gram of the sample in 5 ml. of hydrochloric-nitric acid solution in the usual manner. Boil down on a flame until the molybdenum just starts to precipitate. (Oxidizing acids must be present during the ether extraction to keep the molybdenum in the oxidized state; otherwise highly incomplete extraction will result.) Add 10 ml. of hydrochloric acid and heat to dissolve all material that has precipitated. Cool to room temperature. Pour the solution into a clean 150-ml. separatory funnel and wash the flask with 2 ml. of hydrochloric acid, added from a medicine dropper. Reserve the flask. Add 50 ml. of pure ethyl ether, stopper, and shake vigorously to extract the molybdenum—relieving the pressure by opening the stopcock or removing the top from time to time. After the excess pressure has been eliminated shake for a few seconds and then allow the layers to separate. Drain off the lower acid layer into the reserved flask. Add 5 ml. of hydrochloric acid to the separatory funnel and shake for a few seconds. Drain the acid into the flask. Place the flask on an electric hot plate and boil off the ether. Add about 1 ml. of formic acid and heat gently to destroy nitrates. Boil down on a flame to 5-ml. volume. Cool, add 15 ml. of hydroidic-hypophosphorous acid mixture, and continue as directed in the procedure.

Aluminum and Magnesium. Because of the large amount of heat generated during solution of aluminum and magnesium alloys, it is best to add small portions of the sample to the acid in the flask while the latter is resting in an ice bath. Even with these precautions enough acid may boil off to permit hydrolysis to take place. In view of this and because of the fact that some of these alloys contain considerable amounts of silicon, it is often more convenient to limit the sample size to 0.5 gram.

Nickel. To analyze metallic nickel, dissolve 1 gram of the sample in 10 ml. of nitric acid, boil off all the nitric acid, bake on a flame until most of the nitrates have been converted to oxides, cool, add 10 ml. of hydrochloric acid, heat to dissolve all the salts, destroy the nitrates, and proceed in the usual manner.

Chromium, Silicon, Tungsten, and Zirconium. Materials that are not soluble in nitric or hydrochloric-nitric acid mixtures cannot be analyzed by the recommended method. If the materials are alloyed sufficiently to permit solution or disintegration, an analysis can usually be performed. In some instances it may be possible to resort to a preliminary alkaline fusion.

Table I. Calibration Curve Data

No.	Sulfur, y	% Transmittancy
1	0	98.00
2	10	64.00
3	20	42.75
4	30	25.50
5	40	16.25
6	50	50

DISCUSSION

During the development of the method, spectrophotometric investigation of the lead sulfide sol showed that the transmittancy decreases with decreasing wave length, which suggests that the effect measured may be, at least in part, light scattering rather than light absorption. At 350 m μ or thereabouts the blank, which consists of a mixture of lead nitrate, ammonium citrate, ammonium iodide, and ammonium chloride in dilute ammonium hydroxide solution, begins to exhibit absorption which becomes very marked at about 270 m μ (anions?). In order to avoid this interference, quantitative measurements are best made at a wave length in the region of 370 mµ. Beer's law is followed very well.

The quantitative reduction of sulfate to sulfide is difficult to achieve under the conditions employed in the present method. Several things influence the speed and completeness of the reduction. Among them are acid concentrations, time and temperature of distillation, rate of flow of nitrogen during distillation, etc. Because of the empirical nature of the method, therefore, it is necessary to standardize against sulfate instead of sulfide and to control all important variables.

Extreme precautions must be taken to ensure that none of the distilled sulfide is precipitated previous to the addition of the lead citrate solution; otherwise low results will be obtained due to agglomeration of the sol. Precipitation of the sulfide can usually be recognized visually, but it is safer to rely on the photometer for confirmation. When contamination of the distillate by metal ions is suspected it is best to transfer the distilled sample to a clean absorption cell and photometer as quickly as possible without dilution with water. If the reading is less than 100% T, contamination is indicated. A sample thus tested cannot be used for an analysis, because air oxidation of the sulfide is rapid.

During the development of the present method it was noted that serious contamination of the distillate with lead was encountered in the analysis of Bureau of Standards sample of lead base alloy No. 53b. The cause of this trouble was finally found to be associated with the excess formic acid present in the solution after the destruction of the nitric acid. Apparently some volatile organic compound of lead is formed under the conditions existing at the time of the sulfide distillation. Attempts to eliminate the lead contamination by the use of various types of condensers or liquid traps failed. The only way to prevent contamination was to boil off the formic acid previous to the sulfide distillation.

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Further investigation on the influence of formic acid showed that the effect noted with lead could be detected in the analysis of many of the other metals under investigation. From Table III it will be seen that although the deleterious effect is not so pronounced as it is with lead, it cannot be ignored in accurate work. Oddly enough, very little lead appears to distill from solutions of lead-tin solders. When analyzing metals such as germanium, tin, arsenic, and antimony (whose sulfides are soluble in ammonium hydroxide), and several other metals such as molybdenum, removal of the formic acid will not be necessary. In such cases it will suffice to boil the solution down to 5 ml. after destruction of the nitric acid and before the addition of the hydriodic hypophosphorous acid mixture.

In the analysis of samples containing materials that precipitate during or after solution in nitric or nitric and hydrochloric acid solution, some of the nitrate may be occluded in the precipitate and thus escape destruction by the formic acid. The subsequent treatment with hydriodic-hypophosphorous acid mixture may free some or all of this nitrate and low results for sulfur will be obtained because some of the sulfide will be oxidized by the oxidizing acids that distill over. One common source of trouble is the hydrolysis of metal ions during solution of the sample. Hydrolysis of iron, aluminum, or tin can be prevented (or eliminated) by heating with additional hydrochloric acid. Materials such as lead, silicon, tungsten, and germanium precipitate during solution in the recommended hydrochloric-nitric acid mixture. Experience has shown that no difficulty is encountered with lead alloys as long as solution is made with hydrochloric-nitric acid mixture. On the other hand, when the lead alloy is dissolved in nitric acid, and hydrochloric acid is added subsequently, appreciable amounts of nitrate are occluded in the precipitated lead chloride. The only way to eliminate this condition is to add sufficient hydrochloric acid to prevent the precipitation of the lead chloride during the destruction of the nitric acid. Moderate quantities of silicon, tungsten, and germanium do not appear to cause trouble as long as decomposition of the alloy is made with the recommended hydrochloric-nitric acid mixture. If trouble is encountered with larger amounts of these metals, it may be

Table II. Determination of Sulfur in Various Metals and Alloys

No.		Sulfur Found	Sulfur Recovered ^a
	 B. of S. ingot iron No. 55b (0.018% S) B. of S. Mo-W steel No. 132 (0.004% S) B of S. 18 Cr-8 Ni steel No. 101b (0.023% S) Vicalloy (50 Co. 40 Fe. 10 V) Permalloy (55 Fe. 45 Ni) Mo Permalloy (80 Ni, 14 Fe. 5 Mo) Molybdenum metal A.S.T.M. electronic nickel No. H-1400 Cobalt metal B. of S. inc base No. 94 Cadmium metal B. of S. aluminum base No. 85a Magnesium metal OF HC copper metal Copper metal B. of S. manganese bronze No. 62a Bismuth metal B. of S. solder No. 127 Solder sample B. of S. tin base No. 54c Germanium metal Arsenic Antimony metal 		γ γ ··· 25 24 23 ··· 25 24 ···
304	Setemum	0.0000	20

Amount of sulfur recovered over that present in sample when 25 γ of

sulfur were added. • Values obtained by American Smelting and Refining Co., Barber, N. J., using an independent method were 0.0050% S for copper and 0.0015% S for solder.

d 1.3 grams of B. of S. No. 83a As₂O₃ analyzed.
 d 1.8 grams of H₂SeO₃ analyzed.

necessary to remove the oxides by filtration before treatment with formic acid.

When the metal or alloy to be analyzed contains little or no reducible metal ions it is possible to use less hypophosphorous acid in the distillation mixture. On the other hand, in the analysis of metals such as molybdenum, vanadium, iron, copper, or tin the concentration recommended in the procedure must be used in order to assure rapid and complete reduction of the iodine formed. If the iodine is not reduced by the hypophosphorous acid before distillation takes place, some of it may be carried over into the ammonium hydroxide solution, resulting in oxidation of the sulfide when the latter is subsequently distilled over.

If necessary from an economy standpoint, the amount of distillation mixture or the concentration of hydriodic acid therein may be reduced in certain analyses. On the other hand, reduction is more rapid with the recommended distillation mixture and in addition, the latter has been adjusted to ensure solution of 1 gram of lead, tin, or copper during distillation.

EXPERIMENTAL

Typical calibration curve data, obtained as directed in the procedure, are recorded in Table I.

Various metals and alloys were analyzed as directed in the procedure, using the appropriate modifications whenever necessary. Formic acid was removed in all the analyses except that of molybdenum (Table II). In some cases the values given are an average of duplicate or triplicate analyses. In such instances the maximum spread in the analyses was of the order of 1 or 2 micrograms of sulfur. Because of the lack of suitable standards with which to "prove in" the method, it was necessary in many instances to resort to an indirect procedure for checking the method. This consisted of analyzing two samples of the metal or alloy, to one of which were added 25 micrograms of sulfur in the form of potassium sulfate. (The metal sample was added to a flask in which a 5-ml. aliquot of standard potassium sulfate had been evaporated nearly to dryness.) If the difference in the quantity of sulfur obtained in the two analyses was close to 25 micrograms, it was assumed that the method was satisfactory. The percentages of sulfur found from the first analysis are listed in the next to the last column of Table II. The differences in quantity of sulfur obtained in the first and second analysis are listed in the last column of Table II.

In order to investigate the effect of formic acid, several metal samples were dissolved and distilled as directed in the procedure. Upon completion of the distillation the solution in the volumetric flask was quickly transferred to a clean absorption cell without adding lead citrate or diluting to 25 ml. and photometered at 370 m μ . The process was repeated, with the exception that the excess formic acid was not boiled off. Instead, the solution was boiled down to 5 ml. after the destruction of the nitric acid. The results are recorded in Table III.

Table III. Effect of Formic Acid

No.	Sample	Formic Acid Present	Formic Acid Expelled
		% T	% T
1	B. of S. ingot iron No. 55b	98	100
2	A.S.T.M. electronic nickel No. H-1400	98	100
3	B. of S. zinc base No. 94	98	100
4	OFHC copper metal	96	100
5	Bismuth metal	96	100
6	B, of S. solder No. 127	9 8	100
7	B. of S. lead base No. 53b	85	97
8	Lead (as PbCl ₂)	89	98

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Determination of Zinc Oxide as a Residual of Zinc Powder

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A simple technique, which may be applicable in other cases, has been devised for determining the zinc oxide on powdered zinc. The powder was spread on a copper boat, covered, wrapped tightly in annealed copper foil, and heated in vacuum at 450° C. In this way, the zinc was completely removed and the zinc oxide could be brushed off and weighed on the microbalance.

I N 1946, this laboratory undertook to isolate, identify, and determine the zinc oxide present as a film on fine, reagent grade zinc powder. This objective was accomplished by obtaining the zinc oxide as a residual after the metal had been completely removed by a combination of physical processes carried out under conditions designed to minimize oxidation and loss of oxide by entrainment. The technique employed is new and may prove useful in other cases.

EXPERIMENTAL METHOD

The weighed sample of zinc powder (ca. 200 mg.) is spread evenly on the center portion of the "boat," which is made by splitting thin-walled (ca. 0.08 cm.) copper tubing (see Figure 1). After the boat has been covered with a similar section of tubing pressed into place, it is tightly wrapped in annealed copper foil about 0.003 cm. thick, the edges of which are folded over. Before being used, all copper is hydrogen-fred to remove oxide. Up to three wrapped boats are then stacked, and inserted in the Pyrex firing tube, and the apparatus (Figure 2) is assembled for a run. The tube is flushed for 10 minutes with line hydrogen, evacuated with a good oil vacuum pump for 10 minutes, flushed with line hydrogen for an hour (less would probably suffice), and then reconnected to the pump. The temperature of the furnace is next raised to 450° C. and held there for 30 minutes to complete the separation of zinc and zinc oxide. Furnace and tube are now allowed to cool, whereupon air is readmitted. After the boats have been removed and opened, the loosely adhering zinc oxide