PART I. PREPARATION OF THE SOLUTION

GENERAL DISCUSSION.

The attempt has been made to devise a systematic method of preparing the solution of the substance for analysis, which shall be uniform for all substances, which in the case of those ordinarily met with shall be as rapid as possible, and which shall be so complete as to effect the solution of substantially all known substances. Heretofore little attention has been given to the development of such a definite, uniform plan of treatment, it being assumed that the analyst has the experience necessary to enable him to select, on the basis of the known general character of the substance or of a series of preliminary tests in the dry way, the most suitable method to employ for its decomposition. Yet more experience is required for this than for the ordinary group separations; and there seems to be no reason whatever why this important and difficult part of the analytical process should not be treated in the same systematic way as are the separations and tests for the various elements.

The general character of the plan here presented for accomplishing this end will be readily seen from the "Tabular Outline" given below. The only preliminary test required is one for the presence of organic matter and water, which is made by heating the substance in a closed tube; thus are eliminated the time-consuming blowpipe tests usually recommended, the success of which can be assured and the true significance interpreted only after much experience. For substances found to contain organic matter a special treatment with nitric and sulphuric acids is described by which the organic matter is destroyed. Other substances are treated first with water, and, if this does not cause complete solution, immediately after with strong nitric acid; and any residue still remaining is boiled with hydrochloric acid and *aqua regia,* in order to remove a few substances, such as manganese and lead peroxides, mercuric sulphide, gold, and platinum, which are attacked by these acids, but not by nitric acid.

In the treatment of the residue that may remain unattacked by these acids lies the main difference between our process and that ordinarily recommended in text-books on qualitative analysis; for, as shown in Table II, any such residue is heated with sulphuric and hydrofluoric acids instead of being fused with an alkaline carbonate. By this modification the process of preparing the solution is much simplified in the great majority of cases; for silica is thereby detected and eliminated at the start, and almost all silicates are decomposed, yielding at once either a complete solution, or, if lead, barium, strontium, or much calcium is still present, a residue of their sulphates which can readily be decomposed by boiling with sodium carbonate solution. An even more important advantage of this method, however, is that no foreign metallic elements are introduced;

while, when a fusion is made, alkali elements are introduced from the flux, and aluminum, calcium, and silica from the porcelain crucible, which ordinarily must be used, owing to the possible presence of reducible metallic elements, thus making it necessary to employ other special methods for the detection of these elements. Objection may be raised to the use of hydrofluoric acid because of its being an expensive and irritating reagent and because it must be handled in platinum vessels, thus making it hardly practicable for the use of large classes of beginners. This last consideration would make it desirable to describe in a text-book on the subject the usual method of fusion with an alkaline carbonate as an alternative procedure, which might be used under circumstances which do not permit of the simpler and more satisfactory method with hydrofluoric acid. But we wish to express the conviction that when the subject of qualitative analysis is studied as a branch of analytical chemistry, and not merely as a means of imparting a certain additional chemical knowledge, it ought to be pursued under the same conditions with respect to accuracy of manipulation and availability of facilities as is customary in courses upon quantitative analysis. For the inability to make a good qualitative analysis is a common source of error in quantitative analytical results; and lack of thoroughness in the instruction in qualitative analysis often develops careless and inaccurate habits of work. We have therefore aimed to develop the scheme of analysis best adapted to the purposes of the analyst, and have not hesitated to avail ourselves of the special methods and reagents commonly used only in quantitative work when a more reliable or simpler process could thereby be developed.

Only few substances, especially a few silicates and native oxides, fail to be dissolved by the treatment with sulphuric and hydrofluoric acids; and it is very rare that any further operations are necessary. But to provide for these special cases it is directed to fuse any residue with alkaline carbonate and nitrate, which can now safely be done in a platinum crucible; and, finally, to fuse any residue still remaining (which probably consists only of aluminum, tin, or titanium oxide) with potassium hydroxide.

TABULAR OUTLINE

In the "Tabular Outlines" the enclosure of a symbol in brackets shows that the element may divide itself between the residue and solution in the operation immediately preceding. The symbols of the anhydrous substances are given, without reference to the actual state of their hydration in the residue or precipitate.

TABLE I.

PREPARATION OF THE SOLUTION

Determine by preliminary tests whether the substance contains organic matter (P. 1): and if not, whether it dissolves completely in water and forms an acid or neutral solution (P. 3).

SUBSTANCES CONTAINING ORGANIC MATTER: *Heat with H_2SO_4 and HNO_3 to destroy organic matter, evaporate off HNO_3, add water (P. 2).*		SUBSTANCES SOLUBLE IN WATER FORMING A NEUTRAL OR ACID SOLUTION. *Dissolve in water, add HCl (P. 11).*		OTHER SUBSTANCES *Heat with HNO_3, evaporate, dry, add dilute HNO_3 (P. 3).*			
Residue. *See Table II. below.*	Solution: *Add HCl (P. 2).*			Solution: *Add HCl (P. 3).*		**A.** Residue from alloys: Sb_2O_5, SnO_2, $[P_2O_5]$, $[As_2O_5]$, SiO_2, $[TiO_2]$, WO_3, C, Au, Pt, Ir, etc.; some iron alloys.	
	Precipitate: AgCl. *Confirm by P. 15.*	Filtrate: All elements except Ag. Cr, Pb, Ba, Sr. *Pass in H_2S (P. 21).*	Precipitate: AgCl, HgCl, $[PbCl_2]$, [TlCl]. *(P. 12).*	Filtrate: All elements except Ag. *Pass in H_2S (P. 21).*	Precipitate: AgCl, $[PbCl_2]$, [TlCl]. *(P. 12.)*	Filtrate: *Evaporate;* add HCl *(P. 4).*	**B.** Residue from other substances: oxides under **A** above and substances under **B** in Table II.; also MnO_2, PbO_2, and HgS. *Heat with HCl and HCl + HNO_3, evaporate, dry, add dilute HCl (P. 4).*
					Solution: All elements except Ag. *Pass in H_2S (P. 21).*		Residue: *See Table II. below.*

TABLE II.

PREPARATION OF THE SOLUTION (CONTINUED).

RESIDUE UNDISSOLVED BY ACIDS FROM TABLE I.

A. From alloys: [SnO_2], SiO_2, TiO_2. WO_3. (C, Ir, etc., some Fe alloys).[1]

B. From non-metallic substances: oxides under **A**; also AgCl, CaF_2, MoS_2, many silicates, the sulphates of Pb, Ba, Sr, native Al_2O_3, $FeO.Cr_2O_3$.

C. From substances containing organic matter: substances under **B** (except CaF_2); also Sb_2O_5, $BiOSO_4$, $Cr_2(SO_4)_3$, $CaSO_4$.

Heat with H_2SO_4 and HF, evaporate to expel HF, dilute, boil (P. 5).

Gas: SiF_4. PRESENCE OF SILICON.	Solution: All elements except Pb, Ba, Sr. *Pass in H_2S (P. 21).*	Residue: Pb, Ba, Sr, [Ca], [Bi], [Cr], as sulphates; Sb_2O_5, WO_3; native SnO_2, Al_2O_3, TiO_2, $FeO.Cr_2O_3$: some silicates. *Boil with Na_2CO_3 solution (P. 6).*		
		Solution: Na_2WO_4. *Test for tungsten (*P. 6a).*	Residue: Pb, Bi, [Ba], Sr, Ca as carbonate; [$BaSO_4$], other substances except WO_3 as above. *Heat with HCl (P. 6).*	
			Solution: Pb, Bi, Sb, Cr, [Ba], Sr, Ca as chlorides. *Pass in H_2S (P. 21).*	Residue: [$Cr_2(SO_4)_3$], [$BaSO_4$], MoS_2, native oxides and silicates as above. *Fuse with Na_2CO_3 and KNO_3, add HCl, evaporate, add dilute HCl (P. 7).*
				Solution: *Test for all elements except alkalies (P. 21).* — Residue: SiO_2; native SnO_2, TiO_2, Al_2O_3. *Remove SiO_2 with HF; fuse residue with KOH (P.7. Note).*

[1] A *metallic* residue obtained from an alloy is not treated as described in the table, but is best fused with Na_2O_2(P. 4, Note).

A SYSTEM OF QUALITATIVE ANALYSIS

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PROCEDURES AND NOTES

Procedure 1.—If the substance is a solid, note its color, odor, and texture; examine it with a lens to determine whether it appears to be heterogeneous, and, if so, note the appearance of its constituents. Note especially whether it is an alloy or a non-metallic substance. If the substance is an alloy, pass to P. 3. If the substance is not an alloy, to determine whether organic matter or water is present in it, heat gently at first, then strongly, about 0.1 gram of the finely powdered substance in a hard glass tube (of about 0.6 cm. bore and 8 cm. length) closed at one end. Note whether the substance blackens, whether a tarry or aqueous deposit forms on the cold part of the tube, and whether a burnt odor is emitted. If organic matter is thus proved to be absent, pass to P. 3; if proved to be present, pass to P. 2.

If the substance is a solution in water or other volatile liquid, note its odor, test it with litmus paper, and evaporate just to dryness enough to yield a residue of about 1 gram. Test a small quantity of this residue as described in the preceding paragraph. Treat the remainder by P. 3 if organic matter is found to be absent; otherwise, by P. 2.

Notes.—When a complete analysis in the wet way is to be made, it is usually not worth while to make a more extended preliminary examination in the dry way. The closed-tube test is, however, essential, in order to show whether organic matter is present; for certain kinds of organic matter, especially sugars and hydroxy-acids such as tartaric, citric, and lactic acids, prevent the precipitation of the hydroxides of aluminum and chromium in the subsequent analysis, and must therefore be detected and removed. Moreover, a large quantity of organic matter of any kind interferes with the execution of the analysis; for example, with the operations of solution, filtration, and evaporation.

It is also usually desirable to determine whether water is a constituent of the substance, and, if so, whether it is present in large or small proportion. This can be done with a fair degree of delicacy by the closed tube test, provided care be taken to keep the upper part of the tube cool during the first of the heating. The closed-tube test may also furnish a preliminary indication of the presence of certain metallic and non-metallic elements when they are present in considerable quantity.

Procedure 2.—If the closed tube test (P. 1) has shown the presence of organic matter, powder, or cut into small pieces, 1 to 5 grams of the substance (according to the quantity of organic matter present). Add to it in a casserole about 5 cc. H_2SO_4 (1.84); warm gently until the substance is well charred; cool; add slowly, with constant stirring, under a hood, HNO_3 (1.42), until violent reaction ceases; digest for a few minutes on a steam bath, and then heat over a flame, keeping the dish moving, until the substance is thoroughly charred. Cool, again add HNO_3 as before, and heat until thick fumes of H_2SO_4 are evolved; cool somewhat, and add a little HNO_3. Repeat this process till the H_2SO_4 becomes light-colored and remains so when heated strongly.

Evaporate the remaining H_2SO_4 under a hood to about 1.5 cc. Cool and add carefully about 10 cc. water. If there is a residue, cover the casserole and boil the mixture (to extract slowly dissolving sulphates): cool, filter, and wash, first with H_2SO_4 (1.20) and then with a little water, rejecting the washings. (Residue, P. 5.) To the solution add a drop of HCl (1.12). (If a precipitate forms, add more HCl, but only as long as a precipitate continues to separate; filter, wash the precipitate, and test it for silver by P. 15). Dilute the solution to a volume of 40 cc. (Solution, P. 21).

Notes.—This method of destroying organic matter is of very general application, being effective even when such stable substances as paraffin and cellulose are present. Organic matter can also be destroyed by ignition, but this has the disadvantages of volatilizing certain elements, especially mercury and arsenic, and of making some substances very difficultly soluble. When the organic matter consists only of oil, as is the case with an oil paint, it may be better to extract it with ether, especially when it is desired to determine the proximate constituents of the substance.

The residue contains: any substances originally present that have not been attacked by HNO_3 or H_2SO_4, especially silicates; all the lead, strontium, and barium that may have been present in any form, since the sulphates of these elements are insoluble in dilute H_2SO_4; all the silica, since silicic acid is dehydrated and made insoluble by heating with H_2SO_4; some of the calcium, bismuth, antimony, and tin, when these elements are present in moderate quantity, since their sulphates (or oxides) are not readily soluble in dilute H_2SO_4; and substantially all of the chromium, since its sulphate is converted into the insoluble anhydrous form.

After the organic matter is destroyed, the solution is evaporated to about 1.5 cc. and the solution is finally diluted to 40 cc., in order that the concentration of the acid may be right for the subsequent H_2S precipitation.

Procedure 3.—If organic matter is absent (P. 1), reduce the substance to a finely divided form; weigh out into a casserole about 1 gram if it is a non-metallic substance, or about 0.5 gram if it is an alloy.

In case the substance is not an alloy, add to it 10-30 cc. water, heat to boiling, and test the solution with litmus paper. If the substance has dissolved completely and the solution is neutral or acid, treat the solution by P. 11. If there is a residue or if the solution is alkaline, add carefully without filtering 5-10 cc. HNO_3 (1.42), and evaporate just to dryness.

In case the substance is an alloy, pour over it 10 cc. HNO_3 (1.20), cover the dish with a watch glass, heat the mixture on a steam bath as long as any action continues, adding a little HNO_3 (1.42) if action is renewed thereby, or a little water if crystalline salts have separated, and then evaporate just to dryness.

Heat the residue obtained in either case at 120-130° until it is perfectly dry, by keeping the casserole in motion over a flame, or, better, by heating it in a hot closet at that temperature for at least half an hour. Loosen the dehydrated residue from the dish and rub it to a fine powder with a pestle; add to it 5-10 cc. HNO_3 (1.20), cover the dish, and heat on a steam bath

for 10 minutes. Dilute with 20 cc. water, heat to boiling, filter, and wash the residue. (Residue, P. 4). To the solution add 5 cc. HCl (1.20) to precipitate the silver group, filter, and wash the precipitate with a little cold water, adding the washings to the filtrate. (Precipitate, P. 12; filtrate, P. 4, second paragraph).

Notes.—The quantity of the substance taken for analysis should always be approximately known; for a good qualitative analysis should show, not merely the presence or absence of the various elements in the substance, but should enable their relative quantities to be estimated. Since 1-2 mg. of almost any element can be detected by this system of analysis, the presence of 0.1-0.2% of an element will be detected when a gram of substance is taken, and this degree of delicacy is ordinarily sufficient.

When the substance dissolves only partly in water, it is not worth while to filter off the residue and analyze it and the solution separately, unless special information in regard to the soluble constituents is desired. If, therefore, it is known to be partly insoluble in water, it is best treated at once with HNO_3, as is directed in the case of an alloy. If, however, it is completely soluble in water, the addition of HNO_3 is avoided, since it would have to be removed before the subsequent precipitation with H_2S.

If the aqueous solution has an alkaline reaction, the addition of an acid may cause precipitation of any substance held in solution by an alkaline solvent; for example, sulphur or sulphides of the tin group from an alkaline sulphide solution; silver chloride or cyanide from a potassium cyanide solution; silicic acid from sodium silicate solution; or metallic hydroxides from solutions in alkalies. An alkaline solution is, therefore, first treated with HNO_3, and not directly with HCl by P. 11; for the precipitate formed by the latter might contain other substances than chlorides of the silver group.

In dissolving non-metallic substances either HNO_3 or HCl may be first used, each having advantages and disadvantages of its own. HNO_3 dissolves, owing to its oxidizing power, many alloys and sulphides not attacked by HCl, but fails to dissolve certain oxides, especially MnO_2, Sb_2O_3, and hydrated SnO_2, which dissolve in HCl. HCl may cause the precipitation of chlorides of the silver group; while strong HNO_3 on heating oxidizes sulphides partially to sulphates, and may cause the precipitation of lead, barium, strontium, and calcium sulphates; thus in either case making it sometimes impossible to determine whether complete decomposition has resulted. HNO_3 oxidizes mercurous, arsenous, antimonous, stannous, and ferrous compounds to the higher state of oxidation; consequently almost all the antimony and tin will usually be found in the residue insoluble in dilute HNO_3 after evaporation, all the mercury will be in the H_2S precipitate, and sulphur will always be precipitated by H_2S when iron is present. When HCl is used as a solvent, mercury, selenium, and arsenic in the arsenous form would be wholly or partly lost, owing to the volatility of their chlorides, in the subsequent evaporation, which is necessary in order to remove silica. For this last reason, and for the reason that the procedure is a more general one in that it provides for the solution of alloys and of a larger proportion of non-metallic substances and for the isolation of the silver group, the use of HNO_3 is here recommended. In special cases it is advantageous to use dilute HCl instead of HNO_3, especially when the substance dissolves completely in HCl and it is not necessary to evaporate the solution to remove silica.

The nitric acid solution is evaporated to dryness and the residue is heated at 120-130°, in order to remove the silica at this point; for, if it were not removed, it

would appear as a gelatinous precipitate at some later stage of the analysis; thus, if it did not separate earlier, it would be precipitated by NH_4OH together with the iron group and might then be mistaken for aluminum hydroxide. In the case of non-metallic substances which cannot contain silica, the evaporation and heating at 120-130° may be omitted.

By the treatment of alloys with strong HNO_3, all the more common elements are dissolved, except antimony, tin, and silicon. These are oxidized to antimonic acid ($Sb_2O_5.nH_2O$), metastannic acid (nH_2SnO_3), and silicic acid, which separate at once as white amorphous precipitates except when only small amounts of these elements are present. Certain nitrates, especially that of lead, may separate in crystalline form from the strong HNO_3, but these dissolve upon adding water and heating to boiling. *Of the more important rarer elements, titanium and tungsten, like antimony and tin, separate in the form of insoluble hydroxides; in the case of tungsten, tungstic acid (H_2WO_4) separates as a dense precipitate of a yellow color.

In the case of an alloy the evaporation to dryness and heating at 120-130° serve to partially dehydrate the hydroxides of silicon, tin, antimony, titanium, and tungsten, whereby they are rendered nearly insoluble in HNO_3, and thus make possible a conclusion in regard to their presence or absence. If after having thoroughly dried the mixture at this temperature there is no residue insoluble in the HNO_3 (1.20), it shows the absence of silicon, tin, and tungsten in quantity as large as 1 mg., and that of antimony and titanium in quantity as large as 2 or 3 mg. The fact must not be overlooked, however, that in the dehydrated form even a very small residue or slight turbidity may correspond to an appreciable quantity of one of these elements. Therefore, if no residue can be seen, rub the sides of the dish gently with the rubber-covered end of a glass rod, pour into a small flask, allow the liquid to stand 2 or 3 minutes, and note whether there is any residue whatever. The knowledge that tin is absent is helpful, since the subsequent procedures for the detection of this element may be omitted. The subsequent procedures for antimony may, in the absence of a residue, also be omitted, provided quantities as small as 3 mg. are not to be tested for. In addition to the hydroxides named above the residue may also contain a considerable quantity of stannic phosphate or arsenate when tin and phosphorus or arsenic are simultaneously present, or of bismuth hydroxide when both antimony and bismuth are present; also small quantities of various other elements enclosed in a residue consisting of those already mentioned.

The hydroxides referred to in the last two paragraphs usually separate also in the treatment of non-metallic substances with HNO_3 when the corresponding elements are present; but the non-existence of a residue must not, except in the case of silicon, be regarded as conclusive evidence of their absence in such substances, for acid radicals may be present which by combination with the hydroxides cause them to remain in solution; thus the presence of chloride or sulphate might cause a considerable quantity of tin, antimony, or titanium to dissolve, while that of phosphate might lead to the solution of even a large quantity of tungsten.

A black or metallic residue insoluble in HNO_3, obtained in the case of an alloy, may contain carbon or carbides, certain alloys of iron, such as ferrochrome or ferrosilicon, gold, or any of the platinum metals. If there is no such residue, it shows the absence of gold and platinum.

If the substance is non-metallic, the residue insoluble in HNO_3 probably consists of one or more of the following substances: the partially dehydrated hydroxides of tin, antimony, silicon, titanium, and tungsten; the native or ignited oxides of the same elements, of aluminum, and of chromium; anhydrous chromic salts; the peroxides of manganese and lead; the sulphates of barium, strontium, and lead; the

sulphides of mercury and molybdenum; silica; the silicates and fluosilicates of many elements; fluoride of calcium; the halides of silver and lead; the phosphates of tin and of rare earths; ferrocyanide of iron; sulphur; carbon; silicon carbide.

Procedure 4.—To the residue insoluble in HNO_3 (P. 3) in a casserole add gradually 5-10 cc. HCl (1.20), and heat as long as action continues, adding more acid if necessary. If the substance does not dissolve completely in HCl, add to the mixture without filtering one-third its volume of HNO_3 (1.42), and heat gently as long as action continues, adding more of the acids if necessary.

To this solution in HCl alone, or in HCl and HNO_3, without filtering off any residue, add the filtrate obtained in P. 3, and evaporate the mixture nearly to dryness. In order to expel the HNO_3, moisten the residue with 2-5 cc. HCl (1.20), and evaporate to dryness. Thoroughly dry the residue by heating it at 120-130° in a hot closet or by keeping it in motion over a small flame. Add to the residue 4 cc. HCl (1.12), measured in a small graduate, and about 20 cc. water; boil gently for a few minutes if there is a residue; filter, and wash the residue thoroughly with boiling water. Pour the filtrate into a graduate and add enough water to make its volume 40 cc. (Residue, P. 5; solution, P. 21).

Notes.—Of the substances that may be present in the residue undissolved by HNO_3 (see P. 3, Notes) the peroxides of manganese and lead are reduced and dissolved by concentrated HCl; antimonic acid, stannic phosphate, and much metastannic acid are also dissolved by it. Upon the addition of HNO_3, whereby the strongly oxidizing mixture known as *aqua regia* is produced, gold, platinum, and mercuric sulphide are entirely dissolved; and silver compounds, such as AgBr, AgI, and AgCN, are converted into AgCl. The chloride of silver and the sulphates of strontium and lead dissolve in large quantity in the concentrated acids, but only in much smaller quantity in the small amount of dilute HCl added after the evaporation. Some of the other substances that may be in the residue, especially the oxides and certain silicates, are slowly attacked by the strong acids, but the solvent action is not rapid enough to make this a practicable method.

If the original substance was an alloy, a residue after the treatment with HCl and HNO_3 probably consists of metastannic, silicic, titanic, or tungstic acid; or of carbon, a platinum metal, or an alloy of iron with chromium, silicon, etc. It is best treated with H_2SO_4 and HF by Procedure 5, in order to test for and remove silica and to dissolve metastannic and titanic acids. If a black or metallic residue still remains, it may be tested for graphite by rubbing a dried portion on the fingers or on paper; and to bring it into solution the remainder may then be fused with Na_2O_2 in a nickel crucible, the mass treated with water and HCl, and the solution analyzed as usual, except that nickel cannot be tested for. For a description of this process and the results attained by it, see A. A. Noyes, "System of Qualitative Analysis Including Nearly All the Metallic Elements," Part I, Procedure 13. *Technology Quarterly*, **16**, 113, 1903).

The solution is evaporated to render insoluble silicic acid which may have come from the decomposition of silicates, and to remove the large quantity of acid which would otherwise interfere with the H_2S precipitation. The evaporation with HCl serves, moreover, to remove HNO_3, which, if present in large quantity, would destroy the H_2S with liberation of sulphur. Since the success of the separation by

H_2S of the copper and tin groups from the iron group requires a proper concentration of acid in the solution, a measured quantity of HCl is added and the solution is diluted to a definite volume.

If the original substance was an alloy and a large, non-metallic residue remains after treatment with HNO_3 (P. 3), it is sometimes advantageous to analyze the residue separately by the following procedure, by which a large quantity of metastannic acid is more readily dissolved: Add to the residue in a casserole 3-4 cc. concentrated H_2SO_4, and heat under the hood until the acid has evaporated to a volume of about 2 cc. Cool, add an equal volume of water, cool again, add 5 cc. HCl (1.12) to dissolve antimonic oxide, and heat to boiling. Cool completely, filter if there is a residue (which may consist of silicic or tungstic acid), and add the acid solution drop by drop, with constant shaking, to a mixture of 10 cc. ammonium monosulphide, 1 cc. ammonium polysulphide, and 10 cc. NH_4OH (0.90) in a flask. Cover the flask and digest for a few minutes on a steam bath. Filter out the precipitate, which may consist of titanium hydroxide or small quantities of sulphides of the copper and iron groups. Dilute the filtrate, and make it slightly acid with HCl. Shake to coagulate the precipitate, filter, and wash with hot water. Analyze the precipitate for the tin group by P. 42; reject the filtrate or test it for phosphate with molybdic acid.

Procedure 5.—Transfer to a platinum crucible the residue after treatment with acids (P. 2 or P. 4), add 2 cc. H_2SO_4 (1.84) from a graduate, heat with a moving flame until white fumes are given off, and cool completely. To test for silica, add carefully from the loop of a platinum wire, pure 40% HF drop by drop until 5-6 drops have been added, and warm the mixture over a steam bath. (Formation of gas bubbles, presence of SILICA).

Then add about 5 cc. more pure 40% HF, cover the crucible with a platinum cover, digest on a steam bath for about 15 minutes unless the residue dissolves more quickly; remove the cover and evaporate carefully until white fumes of H_2SO_4 are given off, heating the sides of the crucible with a moving flame, or better, with a ring-burner to avoid spattering. [Unless it is known from the presence of solid substance at this point or from previous observations that the residue treated with H_2SO_4 and HF contained other constituents than silica, determine this by evaporating off the H_2SO_4 under a hood, taking care not to ignite the residue. If a significant residue remains, add from a graduate 1.5 cc. H_2SO_4 (1.84), and heat until the residue is redissolved, not allowing the acid to evaporate]. Cool, pour the contents of the crucible into 10 cc. water, and rinse out the contents with a little water. Boil to dissolve slowly dissolving sulphates; cool, shake, filter, and wash the residue, first with H_2SO_4 (1.20) and then with a little water, rejecting the washings. (Residue, P. 6). To the filtrate add HCl drop by drop only as long as a precipitate forms; filter, wash the precipitate, and test it for silver by P. 15. Dilute the filtrate to a volume of 40 cc., treat it with H_2S by P. 21, subsequently testing for all the metallic elements except lead, barium, and strontium.

Notes.—The test for silica or silicate depends on the formation of SiF_4, gas, which is insoluble in strong H_2SO_4, but dissolves in water in the presence of HF with formation of fluosilicic acid, H_2SiF_6. With free silica the evolution of gas takes place in the cold; but with slowly decomposing silicates, such as feldspar, the test is obtained only upon warming. A few silicates are not acted upon by HF and H_2SO_4, and, of course, do not show the test for silica at this point. The test is delicate enough to enable 1 mg. of silica, whether free or in a decomposable silicate, to be detected. Moreover, after the substance has been treated with acids as in P. 4 and warmed with H_2SO_4, an evolution of gas with HF is not produced with the compounds of any element other than silicon (not even with those of titanium, niobium, and tantalum, which form somewhat volatile fluorides). It should be borne in mind that a small quantity of silica will be introduced if ordinary filters (which have not been washed with HF) have been employed and have been destroyed by acids or by ignition, or if a strongly alkaline solution has been boiled in glass vessels, or if a substance has been fused with sodium carbonate in a porcelain crucible.

In handling cold HF solutions, vessels and funnels of celluloid or paraffin or of glass coated with paraffin may be used; but platinum vessels must be employed when the solutions are to be heated. Platinum is so slowly attacked by hot concentrated H_2SO_4 that even when 2-3 cc. of the acid are rapidly evaporated in a crucible less than half a milligram passes into solution; but, if the acid is boiled for 10-15 minutes in a covered vessel, 2 or 3 mg. may be dissolved, and would be precipitated subsequently by H_2S.

The digestion with HF decomposes most silicates and dissolves silica (and much titanium oxide). The subsequent evaporation with H_2SO_4 expels the excess of HF and decomposes the fluorides produced, as well as some other substances that may have been left undissolved by the HNO_3 and HCl. The H_2SO_4 solution is diluted with a small quantity of water so as to cause the complete precipitation of $BaSO_4$, $SrSO_4$, and $PbSO_4$. These sulphates are moderately soluble in strong H_2SO_4 and may not appear till after dilution. The addition of much water is avoided, since $SrSO_4$ and $PbSO_4$ are somewhat soluble in water; and the residue is washed with dilute H_2SO_4 for the same reason. The solution is boiled so as to dissolve anhydrous sulphates, such as those of aluminium and iron.

The residue insoluble in dilute H_2SO_4 contains as sulphates all the barium, strontium, and lead, and all of the calcium in excess of 5-10 mg., left undissolved by HNO_3 and HCl; more or less of the chromium (according as the H_2SO_4 has been more or less strongly heated) as a pink anhydrous sulphate; and part of the bismuth as basic sulphate and antimony as antimonic hydroxide, when much of these elements were left undissolved by the previous treatments with acids. The residue may also contain still undecomposed substances, especially the following; silver chloride; corundum, Al_2O_3; chromite, $FeCr_2O_4$; cassiterite, SnO_2; rutile, TiO_2; tungstic oxide, WO_3; molybdenum sulphide, MoS_2; some anhydrous silicates and fluosilicates, such as cyanite or andalusite (Al_2SiO_5) and tourmaline; graphite and carbides.

If the presence of silver is shown by the addition of HCl, the residue insoluble in dilute H_2SO_4 is likely to still contain AgCl, which is only slowly decomposed by hot concentrated H_2SO_4. In order to dissolve this, add to the residue in a small casserole 3-5 cc. concentrated H_2SO_4, heat until white fumes are given off, cover the dish with a large watch glass, and boil gently for 5-10 minutes. Cool, and treat as described in the last paragraph of the above procedure. If AgCl is not completely removed in this way, its presence will be shown by a blackening of the residue upon boiling with Na_2CO_3 solution in P. 6; in such a case it must be removed by further

treatment with H_2SO_4 before a fusion with Na_2CO_3 is made in a platinum crucible (P. 7). By this treatment with boiling H_2SO_4, Al_2O_3 and TiO_2, if present in the residue, are also dissolved in large quantity.

If the use of a platinum crucible or of hydrofluoric acid is impracticable, the residue insoluble in HCl and HNO_3 may be fused in a porcelain crucible with a mixture of Na_2CO_3 and K_2CO_3, instead of being treated by P. 5-7. This is, however, a far less satisfactory method of analysis for the following reasons. Compounds of the alkali elements are used as a flux, and aluminum, calcium, and silica are introduced from the porcelain crucible, so that these elements cannot be tested for in the insoluble residue. Moreover, the treatment with HF and H_2SO_4 is almost always a shorter process, since when the residue consists only of silica, as is often the case with minerals, no further treatment is necessary, and since in other cases there is often no residue to be boiled with Na_2CO_3 solution (P. 6) and seldom one to be used with Na_2CO_3 (P. 7). A fusion in a platinum crucible with alkali-metal carbonate would be less objectionable; but this is not possible unless reducible metallic elements are known to be absent in the residue.

Procedure.—Transfer the residue insoluble in H_2SO_4 (P. 5) to s casserole, add about 25 cc.[1] saturated Na_2CO_3 solution, cover the casserole and boil gently for 10 minutes. Filter and wash the residue thoroughly. (Filtrate, reject or test for tungsten by *P. 6a). Heat the residue with 5 cc. HCl (1.12), measured in a graduate, and 10 cc. water; filter, wash the residue, and treat it by P. 7. Dilute the solution to 40 cc. and treat it with H_2S by P. 21, subsequently testing it only for lead, bismuth, antimony, chromium, barium, strontium, and calcium.

Notes.—The boiling with Na_2CO_3 converts into carbonates the sulphates of lead, calcium, strontium, and bismuth completely, and at least 80% of the sulphate of barium, even when large quantities of them are present. A second treatment, which should be applied to the residue if there are indications that barium is present, completely decomposes $BaSO_4$. The carbonates dissolve readily in HCl. Anhydrous chromic sulphate, which is left undissolved by dilute H_2SO_4 (P. 5) as a fine pink or gray powder, is slowly changed by boiling with Na_2CO_3 to a greenish blue hydroxide which dissolves in the HCl, leaving behind the still undecomposed sulphate. Antimonic oxide dissolves only to a small extent (2-4 mg.) in the Na_2CO_3 solution but dissolves upon boiling with HCl. Tungstic oxide passes into the Na_2CO_3 solution as sodium tungstate (Na_2WO_4).

Any residue insoluble in HCl can therefore consist only of barium and chromic sulphates or of some of the original substance still undecomposed, consisting, probably, of one of the native oxides or silicates mentioned in P. 5, Notes. Such a residue will seldom be obtained; and if so, it can ordinarily be rendered soluble by fusion with Na_2CO_3 and KNO_3 (or with KOH) as described in P. 7 (or P. 7, Note).

The residue undissolved by dilute H_2SO_4 after the treatment with HF (P.5) is first boiled with Na_2CO_3 solution and not at once fused, since it is necessary to remove the reducible elements, lead, bismuth, and antimony, before a platinum crucible can be used for the fusion. Moreover, the boiling with Na_2CO_3 solution makes subsequent fusion unnecessary when the residue consists only of sulphate of lead or of an alkaline-earth element.

[1] See, however, *P. 6a, Note, if a small quantity of tungsten is to be tested for.

*Procedure 6a.—Acidify the Na_2CO_3 solution (P. 6) with HNO_3, evaporate almost to dryness, add 1-2 cc. HNO_3 (1.20); add enough water to dissolve the salt, boil, and cool. (Yellow precipitate, presence of TUNGSTEN). Filter and wash the precipitate, rejecting the solution. Pour through the filter 2 cc. NH_4OH (0.96) to dissolve any H_2WO_4, acidify the filtrate with HCl (1.20), and add a few granules of zinc. (Blue color, presence of TUNGSTEN).

Notes.—When HNO_3 is added to a tungstate solution a hydrated tungstic acid separates as a white flocculent precipitate, which changes upon boiling to a yellow powder (H_2WO_4). The test is not very delicate in the presence of a large amount of salt; when 25 cc. Na_2CO_3 solution are used, as is directed in P. 6, even 3 mg. of tungsten can barely be detected in this way. Therefore, when tungsten is to be tested for, the residue from P. 5 should first be boiled with a small portion (5 cc.) of Na_2CO_3 solution, and this solution tested for tungsten as described above; under these conditions 1 mg. can be detected. The test is entirely unsatisfactory if H_2SO_4 or HCl is used, in place of HNO_3, in neutralizing the Na_2CO_3; for by these acids a small quantity of tungstic acid is not thrown down as a yellow precipitate.

The blue color obtained upon reduction with zinc, which serves as a confirmatory test for tungsten, is due to a suspended, quickly coagulating precipitate, consisting of a hydrated oxide intermediate between WO_3 and WO_2. Prolonged action of zinc may cause the blue color to disappear, owing to complete reduction to WO_2.

In the Na_2CO_3 solution will usually be found all the tungsten in the substance in excess of 2 mg., which amount remains in solution in the H_2SO_4 (P. 5). When, however, phosphate is also present in the substance, tungsten would not remain as H_2WO_4 in P. 3 and 4, but would pass into the acid solution, owing to the formation of a complex phospho-tungstic acid.

Procedure 7.—Transfer the residue insoluble in HCl (P. 6), with the filter if necessary, to a platinum crucible, heat until the residue is dry or until the filter is destroyed, mix the residue with 5-10 grams of anhydrous Na_2CO_3 and 0.1-0.5 gram of solid KNO_3, cover the crucible, and heat over a powerful burner. After some minutes note whether a perfectly fluid fusion has resulted. If not, heat more intensely over a blast lamp for 10 minutes, adding, if necessary, more Na_2CO_3. Cool, place the crucible in a casserole, add carefully HCl (1.12) till the solution remains strongly acid, evaporate to dryness, and heat at 120-°130° to render silica insoluble; add from a graduate 4 cc. HCl (1.12) and 10-20 cc. water, boil, and filter. Dilute the filtrate to 40 cc., and treat it with H_2S by P. 21, subsequently testing it for all metallic elements except the alkalies. Test the residue for silica by P. 5, and remove it if present; if a residue still remains, treat it as described in the last paragraph of the notes.

Notes.—Of the substances that may be present in the residue which has been boiled with Na_2CO_3 solution, the silicates are decomposed by fusion with Na_2CO_3 alone. But in order to render chromium compounds (and molybdenum sulphide) soluble, they must be oxidized; and for that purpose a little KNO_3 is added. The native and ignited oxides of tin, aluminum, and titanium are only slowly acted upon

by the flux, and remain insoluble with the silica upon the subsequent treatment with acid. $BaSO_4$, if still present, will also remain with the silica; for, though it is converted into $BaCO_3$ and Na_2SO_4 by the fusion, it is formed again when the mass is treated with acid.

Any residue insoluble in dilute HCl probably consists, therefore, only of SiO_2, TiO_2, $BaSO_4$, Al_2O_3, and SnO_2. Such a residue is best treated first by P. 5 and 6, to remove SiO_2 and $BaSO_4$, and any residue still remaining may then be treated as follows: Reduce it to a very fine powder, transfer it to a nickel or silver crucible, dry thoroughly, add 5-10 grams pure solid KOH, and fuse the mixture for 10-20 minutes. Cool, extract with about 30 cc. water, and filter. Neutralize the solution exactly with HCl (1.12). Treat the residue with about 5 cc. HCl (1.12), filter out any residue of undecomposed substance, and unite the solution with the neutral aqueous extract. Treat the mixture by the regular procedure beginning with P. 21, testing especially for tin, titanium, and aluminum. The native and ignited oxides of aluminum, stannic tin, and titanium, if finely powdered, dissolve rapidly in fused KOH; and the aqueous extract contains the aluminum as aluminate and most of the tin as stannate. The residue undissolved by water may consist of black nickel oxide from the crucible, or of stannic hydroxide, potassium titanate, and sometimes other hydroxides coming from the original substance. All of these dissolve in HCl.

CONFIRMATORY EXPERIMENTS AND REFERENCES.

P. 2: Destruction of Organic Matter.—3 grams white flour, 1.5 grams glycerol, 0.5 gram paraffin, and some filter paper were treated in separate experiments, according to the procedure: nearly all the organic matter was decomposed by the first two or three treatments with H_2SO_4 and HNO_3, and after a few more treatments colorless solutions were obtained.

P. 3: Volatility of Mercury and Arsenic Compounds.—Separate solutions containing 1 mg. Hg as $HgCl_2$ in HNO_3, HCl, *aqua regia*, and H_2SO_4, were carefully evaporated just to dryness; the residue was in each case dissolved in a little water, and the solution saturated with H_2S: a precipitate of HgS estimated by comparison at not less than $^2/_3$ mg. Hg was obtained in each case, showing that not much of the mercury had been volatilized. It was found that $HgCl_2$ was not converted into $Hg(NO_3)_2$ by the evaporation with HNO_3.

1 mg. Hg as $HgCl_2$ was heated in a hot closet at 125°, the casserole was washed out with water, and the solution saturated with H_2S: no precipitate was obtained, thus showing that the $HgCl_2$ was completely volatilized.

1 mg. Hg as $Hg(NO_3)_2$ was heated for two days at 125° in a hot closet, dissolved in water, and treated with H_2S: an HgS precipitate resulted, whose size indicated that little or none had volatilized.

10 mg. As as As_2O_3 were added to 10 cc. HCl (1.20), and the solution was boiled vigorously for about 15 seconds; the solution was somewhat diluted and then saturated with H_2S: only 1-2 mg. As as As_2S_3 were precipitated.

The experiment was repeated, except that the HCl solution was evaporated to 2 cc.: scarcely any precipitate of As_2S_3 was obtained. In another experiment the solution was evaporated to dryness: no precipitate of As_2S_3 formed.

A solution of 10 mg. As as As_2O_3 in 10 cc. H_2O and 2 cc. HCl (1.20) was boiled for 30 seconds and H_2S was passed in: a precipitate appearing like that given directly by 10 mg. As was obtained, showing that very little if any arsenic was volatilized. A similar solution of 10 mg. As was evaporated to 2 cc.: it gave with H_2S a precipitate estimated to contain 3 mg. As.

1 and 10 mg. As as As_2O_3 dissolved in 5-10 cc. HCl (1.20) were boiled in covered casseroles, oxidized with bromine water, evaporated to dryness, and dissolved in HCl; the solution was then precipitated with H_2S: the amount of arsenic precipitated was estimated to be nearly as great as that originally taken, thus showing that arsenic in the higher state of oxidation is not volatilized.

Solubility of the Dehydrated Hydroxides in HNO_3.—For this and for a statement as to other substances that the residue may contain, see A. A. Noyes, *Technology Quarterly*, **16**, 121-126 (1903).

P. 4: Action of HCl and HNO_3 on $AgCN$ and AgI.—50 mg. Ag as freshly precipitated AgCN were boiled with 20-30 cc. HCl (1.20): the precipitate dissolved quickly.

To 50 mg. Ag as freshly precipitated AgI were added 10 cc. HNO_3 (1.42), and the mixture was evaporated, diluted, filtered, and HCl was added to the filtrate: a precipitate of AgCl estimated to contain 15 mg. Ag was obtained, showing that AgI is slowly decomposed by HNO_3. The experiment was repeated with 50 mg. Ag as AgCN: no precipitate of AgCl was obtained.

Solubility of Metastannic and Antimonic Acids in H_2SO_4 and HCl.—200 and 400 mg. Sn as metastannic acid, which had been heated for 1 hour in a hot closet at 120°, were treated in separate experiments with 3 cc. concentrated H_2SO_4 as described in the Notes: in the first case all the tin, in the second all but a few milligrams of it, dissolved on boiling the acid for about a minute. The solutions were diluted with 2-3 cc. water and boiled: no precipitate formed. The first solution was cooled and poured into 10 cc. cold water: a solution which remained clear for several hours was obtained, from which a white precipitate separated at once on boiling. To the other solution (containing 400 mg. Sn) were added 5 cc. HCl (1.12) and 50 cc. water: no precipitate appeared, even on boiling. The solution was diluted to 200 cc.: a white precipitate then formed. The precipitates obtained from these solutions dissolved readily in dilute HCl and in concentrated H_2SO_4.

200 mg. Sb as hydrated Sb_2O_3, previously heated at 120°, were boiled with 5 cc. HCl (1.12) for 2 or 3 minutes: a complete solution resulted.

200 mg. Sb as hydrated Sb_2O_5 (heated at 120°) did not dissolve in 3 cc. boiling concentrated H_2SO_4 or on dilution, but dissolved readily when HCl was added as described in the Note. This solution was diluted with 10 cc. water: a slight precipitate formed, which dissolved on the addition of a little HCl and warming.

In another experiment 200 mg. Sn as dehydrated metastannic acid were boiled for about 30 minutes with HCl (1.20): at the end of that time the solid had dissolved nearly, but not quite completely.

Solubility of Metastannic, Antimonic, and Silicic Acids in Ammonium Sulphide.—200 mg. metallic antimony and 300 mg. metallic tin were treated in separate experiments by P. 3 and the procedure described in Note 4: clear solutions were obtained on adding the acid solution to the alkaline ammonium sulphide solution.

The following experiments show that the residue from P. 3 may be treated directly with ammonium sulphide, but that this process is ordinarily a longer one than that described in the Note.

200 mg. Sn as dehydrated metastannic acid, previously heated at 120°, were warmed gently with successive 10 cc. portions of the ammonium polysulphide reagent in a covered casserole for 5-10 minutes, with frequent stirring: in the first treatment considerably more than half of the tin dissolved; after the second treatment only about 20 mg. were left undissolved and two more treatments dissolved this completely.—The experiment was repeated, using colorless ammonium monosulphide in place of the yellow polysulphide: the same results were obtained.

500 mg. Sn as dehydrated metastannic acid were treated with successive 10 cc. portions of yellow ammonium sulphide in a pressure bottle at 70-80°: practically all dissolved in two 10-minute treatments.

200 mg. Sn as dehydrated metastannic acid dissolved in 10 cc. ammonium monosulphide in a pressure bottle at 80° in about 10 minutes, and another portion of about 100 mg. Sn dissolved in the same solution on further heating.

200 mg. Sb as hydrated Sb_2O_5, previously heated at 120°, were treated in a covered casserole with ammonium polysulphide; it dissolved only very slowly and several treatments were necessary to effect complete solution. As with metastannic acid, the use of the pressure bottle hastened the solution, but antimonic acid dissolved even less readily than metastannic acid.

100 mg. dehydrated silicic acid were warmed for 15 minutes with 20 cc. ammonium monosulphide; the filtrate was acidified, evaporated to dryness, and tested for silica by P. 5: very little, if any, gas evolution was obtained, thus showing that SiO_2 is insoluble in ammonium sulphide.—In another experiment only a few milligrams (1-3) SiO_2 dissolved in 30 cc. boiling ammonia (0.96) in 15 minutes.

P. 5: Test for SiO_2 with HF and H_2SO_4.—1 and 2 mg. of dehydrated H_2SiO_3 were treated as described in the first paragraph of P. 5: evolution of gas took place at room temperature and was easily seen in both cases.

1 and 2 mg. SiO_2 as feldspar, which had been well purified from free silica by long-continued boiling with Na_2CO_3 solution, were treated in separate experiments according to P. 5: there was no evolution of gas in the cold, but a distinct one took place on warming.

500 mg. $BaSO_4$, 100 mg. TiO_2, 100 mg. tantalic acid, and 150 mg. niobic acid were treated by P. 5: no evolution of gas was observed in the cold nor on warming, provided the solid had been previously heated with the strong H_2SO_4 to remove air bubbles.

A filter (Schleicher und Schüll, No. 597) 11 cm. in diameter, with an ash stated to be 0.0028 gram, was treated by P. 2, to destroy organic matter, and the residue by P. 5, to test for silica: bubbles of gas were clearly seen.

In a series of experiments an attempt was made to test for silica by adding HF to the dry solid and allowing the SiF_4 evolved to act on a drop of water held in the loop of a platinum wire near the solid. The best conditions were found to be to add less HF than corresponded to the silica present, to allow the reaction to continue until almost all the HF was destroyed, the action being accelerated by stirring with a heavy platinum wire, and then to warm the mixture gently, while holding the drop of water near the solid. Even under these conditions, however, the drop did not become turbid when less than 5 mg. SiO_2 were used, although an evolution of gas doubtless took place, as was shown by a hissing sound.

Action of Hot H_2SO_4 on Platinum.—5 cc. H_2SO_4 (1.84) were evaporated to 2 cc. in an open platinum crucible within 2 or 3 minutes, cooled, diluted with 5-10 cc. water, and H_2S passed into the hot solution for some minutes: a brown coloration appeared quickly, but no precipitate settled out.

5 cc. H_2SO_4 (1.84) were boiled for 15 minutes in a covered platinum dish previously weighed, cooled, diluted, and saturated hot with H_2S: a precipitate of PtS_2 estimated to contain 2-3 mg. Pt was obtained and the dish had lost 3 mg. in weight.

Action of H_2SO_4 and HF on Minerals and Other Substances.—Each of the following substances was treated with the stated result by the following procedure, which is similar to the regular process, P. 4-6, except that in these experiments the substance was digested for a longer time with hot concentrated H_2SO_4. 1 gram was digested for several minutes in a covered platinum dish with 10 cc. HNO_3 (1.42).

3 cc. H_2SO_4 (1.84) were then added, the mixture was evaporated to distinct fuming, and maintained at that point for 10 minutes. 5 cc. HF were added, the mixture was digested for 15 minutes on a water bath, and then evaporated until thick acid fumes were given off; 3 cc. HF were added, and the mixture was again evaporated to fuming. 30 cc. water were added, the mixture was boiled for 15 minutes, cooled, diluted to 100 cc., and the residue washed once by decantation. 30 cc. saturated Na_2CO_3 solution were then poured over the residue, and the mixture was allowed to stand, with frequent stirring, for 15 minutes. The solution was decanted, and the residue washed twice with water, after which it was treated with 30 cc. HCl (1.02). A large residue was left after the final treatment with HCl by cassiterite (SnO_2), emery (Al_2O_3), chromite ($FeO.Cr_2O_3$), rutile (TiO_2), cinnabar (HgS), molybdenite (MoS_2), tourmaline, beryl ($Be_3Al_2Si_6O_{18}$), and columbite ($Fe(Nb,Ta)_2O_6$). About a third of the molybdenite was decomposed by the HNO_3 with separation of some molybdic acid, which dissolved in the H_2SO_4. Cinnabar, rutile, and beryl were much attacked by H_2SO_4, and columbite by HF, but the other substances were attacked not at all, or only very slightly, by any of the reagents.—Fluorspar (CaF_2), chrome yellow ($PbCrO_4$), wulfenite ($PbMoO_4$), and vanadinite ($3Pb_3V_2O_8.PbCl_2$) were attacked by HNO_3 and by H_2SO_4; titanite ($CaTiSiO_5$), garnet (($Ca, Mg. Mn,Fe)_3 Al_2Si_3O_{12}$), a cement, and some slags containing lead or calcium, were attacked by these acids and also by HF. All left, after the treatment with HF and H_2SO_4, a white residue, which, after the treatment with Na_2CO_3, dissolved completely in HCl. The white residue, therefore, contained only insoluble sulphates, such as $PbSO_4$, $CaSO_4$; and the substances were completely decomposed by the treatment with HNO_3, H_2SO_4, and HF—Wolframite (($Fe, Mn)WO_4$), menaccanite ($FeTiO_3$. Fe_2O_3), and prussian blue were decomposed by H_2SO_4, and all left a residue insoluble in dilute H_2SO_4, which dissolved completely, or nearly so, in Na_2CO_3.—Magnetite (Fe_3O_4), cryolite (Na_3AlF_6), basalt, granite, monazite, a uranium ore, and a number of slags were completely decomposed after the treatment with HNO_3, H_2SO_4, and HF, and dissolved completely in the dilute H_2SO_4.

For the action of HF and HNO_3 on some other difficulty soluble native silicates, see *Technology Quarterly*, **16**, 126 (1903).

Solubility of Sulphates in Concentrated and Dilute H_2SO_4.—100 mg. and 150 mg. Ba as $BaSO_4$ were strongly heated with 2 cc. concentrated H_2SO_4: a clear solution resulted in the first case, but not in the second. $BaSO_4$ was precipitated at once when a little water was added.

10, 15, and 20 mg. Ca as $Ca(NO_3)_2$ were added in separate experiments to 20 cc. H_2SO_4 (1.20): with the 20 mg. a precipitate separated at once and with the 15 mg. after about 5 minutes, while with the 10 mg. none formed, even after several hours.

300 mg. Al, 300 mg. Fe, 100 mg. mercuric Hg, and 150 mg. Cu, all as sulphates, were in separate experiments boiled with concentrated H_2SO_4, cooled, diluted, and again boiled as described in the procedure: the anhydrous $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ dissolved completely after about 3 minutes' boiling; the anhydrous $CuSO_4$ and the $HgSO_4$ dissolved at once on warming.

To 100 mg. Cr as $Cr_2(SO_4)_3$ in solution as green sulphate 2 cc. H_2SO_4 (1.84) were added, and the solution was evaporated until thick acid fumes came off; the mixture was cooled, diluted, and boiled, the whole treatment being as in the Procedure: the resulting solution was green, and from its color was estimated to contain 10-15 mg. Cr; the remainder of the chromium was left as a very finely divided light-pink powder (anhydrous $Cr_2(SO_4)_3$).—This experiment was repeated, except that the H_2SO_4 was heated only until slight fumes appeared: no pink precipitate separated, and on boiling with water a clear green solution was obtained.

100 and 200 mg. Cr as precipitated $Cr(OH)_3$ were dissolved in 5 cc. H_2SO_4 (1.84) and 20 cc. water; the solutions were evaporated to about 2 cc., cooled, diluted, again boiled, and filtered: a very finely divided, gray to pink powder (anhydrous $Cr_2(SO_4)_3$) was obtained, which ran through the filter. The precipitate was allowed to settle and the solution was decanted and boiled with NH_4OH: it was colorless and gave scarcely any precipitate of $Cr(OH)_3$. The anhydrous sulphate was boiled for 15 minutes with dilute H_2SO_4; only a few milligrams dissolved. The sulphate was found to be slowly dissolved by a concentrated Na_2O_2 solution owing to oxidation to chromate.

500 mg. Sb as $SbCl_3$, 50 mg. antimonic Sb ($SbCl_3$ previously boiled with HNO_3 and HCl), and 500 mg. Bi as $Bi(OH)_3$ were heated in separate experiments with 3-5 cc. H_2SO_4 (1.84), evaporated to 2 cc., diluted to about 20 cc., and again boiled. With the antimonous salt a crystalline precipitate was obtained on evaporating the H_2SO_4 solution; this precipitate dissolved when the 20 cc. water were added, but an amorphous precipitate formed when much more water was added. The antimonic antimony was precipitated in the concentrated H_2SO_4 as an amorphous powder, and more of this precipitate separated on dilution; the dilute H_2SO_4 solution was filtered and the amount of antimony contained in the filtrate was estimated by precipitating with H_2S to be about 10 mg.; the residue insoluble in H_2SO_4 was washed with water and dissolved in boiling HCl, and to the solution $BaCl_2$ was added: only a slight precipitate of $BaSO_4$ was formed, showing that the residue was an oxide or hydroxide, not a sulphate. In the experiment with bismuth the hydroxide dissolved in H_2SO_4, and a crystalline precipitate (sulphate) separated from the hot concentrated H_2SO_4, but the larger part of this dissolved on adding the water, provided the solution was kept cold; a precipitate (of oxysulphate) appeared when this solution was heated; the filtrate from this was treated with NH_4OH, and a precipitate was obtained which was estimated to contain 20-50 mg. Bi.

Decomposition of Silver Salts by H_2SO_4.—500 mg. Ag as precipitated AgCl, 500 mg. Ag as fused AgCl, 100 mg. Ag as precipitated AgCN, and 100 mg. Ag as precipitated AgI were treated with H_2SO_4 as described in P. 5: there was a residue in each case. HCl was added to the H_2SO_4 solution: a small precipitate of AgCl was then obtained, showing that some of the silver salt had been decomposed. The residues were boiled with 5 cc. H_2SO_4 (1.84) in a covered casserole for several minutes: AgI and AgCN dissolved readily in less than 5 minutes, and almost all the AgCl in less than 10 minutes.

500 mg. Ag as AgCl were boiled with Na_2CO_3 solution (as described in P. 6) for 15 minutes: the AgCl precipitate quickly turned black. The Na_2CO_3 solution was acidified with HNO_3, and $AgNO_3$ added: a precipitate of AgCl, estimated to contain 2 mg. Ag, formed, showing that only this amount of Ag as AgCl had been converted into silver oxide.

Action of H_2SO_4 on Al_2O_3 and TiO_2.—2 grams coarsely powdered corundum, which had been previously digested with HF, and 0.5 gram rutile were in separate experiments boiled with 10 cc. H_2SO_4 (1.84) in a covered casserole for 15 minutes; the mixture was diluted, filtered, and the filtrate made alkaline with NH_4OH: about 50 mg. Al and about half the titanium were precipitated as hydroxides.

100 mg. Al as Al_2O_3, obtained by igniting $Al(OH)_3$, were boiled with 5 cc. H_2SO_4 (1.84) in a covered casserole for 10 minutes: a residue containing 10-20 mg. Al was left undissolved, and this did not dissolve completely on two more treatments with H_2SO_4.—The experiment was repeated with 200 mg. Ti as ignited TiO_2: nearly all of it dissolved in 3-4 minutes.

P. 6: Action of Boiling Sodium Carbonate Solution on $BaSO_4$, $Cr_2(SO_4)_3$, and

Sb_2O_5.—500 mg. Ba as $BaSO_4$ were treated by the procedure: a residue of $BaSO_4$ corresponding to about 30 mg. Ba remained on adding HCl. This residue was treated a second time by the procedure: not more than 1-2 mg. Ba as $BaSO_4$ then remained.

100 and 200 mg. Cr as anhydrous $Cr_2(SO_4)_3$, obtained as described under C. E., P. 5, were boiled with Na_2CO_3 in a covered casserole as described in P. 6: the pink precipitate slowly became greenish blue in color. The Na_2CO_3 solution was acidified with HCl, and $BaCl_2$ added to it: a precipitate of $BaSO_4$ was formed, thus showing that chromic sulphate was being decomposed.

The greenish blue residue from the experiment with 100 mg. Cr (which in contrast to the anhydrous sulphate filtered easily) was boiled with HCl: some chromium dissolved, but the greater part was left as undecomposed (pink) anhydrous sulphate.

The greenish blue residue from the experiment with 200 mg. Cr was boiled for about 2 hours with seven successive portions of Na_2CO_3 solution, and these solutions were tested for sulphate. The sulphate in these portions steadily decreased in amount and the last portion was free from it. The greenish blue residue now dissolved completely in HCl on warming, and the solution gave no precipitate with $BaCl_2$, showing that the chromic sulphate had been completely converted into the hydroxide.

100 mg. Sb as antimonic hydroxide, obtained as described under C. E., P. 5 were boiled with 25 cc. Na_2CO_3 solution in a covered casserole for 15 minutes; the solution was acidified, and treated with H_2S: an orange precipitate of sulphide was obtained which was estimated to contain 3-4 mg. Sb.

*$P.6a$: *Precipitation of H_2WO_4 from Na_2CO_3 Solution by acids.*—1 mg. W as Na_2WO_4 was added in separate experiments to 5 cc. H_2O, to 5 cc. saturated Na_2CO_3 solution, and to 20 cc. Na_2CO_3 solution; HNO_3 was added in excess and the solutions evaporated almost to dryness: yellow H_2WO_4 separated in the presence of HNO_3 alone, but not in the solutions containing $NaNO_3$. The latter were diluted with enough hot water to dissolve the salt, 1-2 cc. HNO_3 (1.20) were added, the solutions were boiled vigorously and then cooled: yellow H_2WO_4 precipitated in the solution containing the smaller amount of salt, but not in the other solution.—The experiment with 20 cc. Na_2CO_3 solution was repeated except that 2 mg. and 3 mg. W (in separate experiments) were taken: no yellow precipitate was obtained with 2 mg., and only a slight one with 3 mg., thus showing that the presence of $NaNO_3$ interferes with the test.

Solutions containing, respectively, 1, 2, 5, 10, and 20 mg. W as Na_2WO_4 in 20 cc. Na_2CO_3 solution were evaporated with excess of H_2SO_4 to strong fuming, diluted to about 15 cc., boiled, and cooled again: no yellow precipitate was formed in any of the experiments.—Solutions containing 2, 3, 5, and 10 mg. W as Na_2WO_4 in 20 cc. Na_2CO_3 solution were evaporated with excess of HCl almost to dryness, diluted to about 15 cc., boiled, and cooled: no yellow precipitate was formed. The final solutions obtained in all these experiments turned blue when some granules of zinc were added, though the color from 1 mg. W in H_2SO_4 appeared only after several minutes.

Reduction of H_2WO_4 with Zinc.—See v. d. Pfordten, *Ber. d. chem. Ges.*, **16**, 508 (1883).

To 10 mg. W as Na_2WO_4 in a test tube were added 5 cc. water, 5 cc. HCl (1.12), and a few granules of zinc: a white precipitate separated when HCl was added, and a deep blue color resulted from the action of the zinc; after half an hour the blue color had changed to a dark brown, and a dark-colored precipitate was suspended in the solution.

Solubility of H_2WO_4 in Acids.—2 mg. W as Na_2WO_4 were treated by P. 3, 4,

and 5 except that no HF was added: a yellow precipitate of H_2WO_4 was obtained on boiling with HNO_3 and was not dissolved by dilute HNO_3 after the evaporation (P. 3); the residue dissolved in HCl (1.20) on boiling, but H_2WO_4 was precipitated on evaporating the *aqua regia* and was not dissolved by the dilute HCl (P. 4). Nearly all the residue dissolved, however, in 2 cc. H_2SO_4 (1.84) and did not re-precipitate on diluting to 20 cc. and boiling (P. 5.—For the solubility of H_2WO_4 in concentrated H_2SO_4 and after dilution, see *Technology Quarterly*, **17**, 249 (1904).

P. 7: Effect of fusing Al_2O_3, SnO_2, TiO_2, MoS_2 with Na_2CO_3 or with Na_2CO_3 and KNO_3.—For the fact that a large residue remains when native Al_2O_3, TiO_2, and SnO_2 are fused with Na_2CO_3, see *Technology Quarterly*, **16**, 127 (1903).

80 mg. Al as Al_2O_3, obtained by igniting precipitated AlO_3H_3 over a blast lamp for 15 minutes, were fused with 8 grams Na_2CO_3 in a platinum crucible over a powerful burner for 20 minutes; 0.2 gram KNO_3 was then added and the heating continued for 10 minutes longer; the fusion was cooled and digested with HCl: only a small residue of unattacked Al_2O_3, corresponding to 5-10 mg. Al, remained. The solution gave no precipitate with H_2S, showing that platinum had not been removed from the crucible.

500 mg. Mo as molybdenite (MoS_2) were fused for 3-5 minutes in a porcelain crucible with 10 grams Na_2CO_3 and the mass treated with water; the black particles of MoS_2 all dissolved during the fusion, and the mass, which had a light red color, dissolved nearly completely in water. HCl was added to the solution: a large black precipitate separated.

150 mg. Mo as molybdenite were fused for about 2 minutes in a platinum crucible with 8 grams Na_2CO_3 and 0.5 gram KNO_3, and the mass was treated with dilute HCl: complete solution resulted; the platinum crucible was not injured.—The experiment was repeated except that the KNO_3 was added after a minute's fusion with Na_2CO_3: the result was the same.

Effect of Fusing Al_2O_3, SnO_2, TiO_2 with KOH.—200 mg. of coarsely powdered corundum (Al_2O_3) that had been previously digested with HF and with concentrated H_2SO_4 and 200 mg. of finely powdered cassiterite (SnO_2) were fused with 10 grams KOH in nickel crucibles for 15 minutes; the mass was extracted with water and the residue heated with HCl: a residue still remained, which was estimated to contain about half the Al_2O_3, but little, if any, of the SnO_2. An analysis was made of the aqueous extract and the HCl solution: the former was found to contain about 50 mg. Al (as aluminate) and 100-150 mg. Sn (as stannate), but no nickel; the HCl solution contained 20-40 mg. Sn, 10-15 mg. Ni, and some Fe as chlorides, but no other metallic element.

1 gram of rutile containing 600 mg. Ti was treated by P. 3, 4, and 5; the residue was fused with KOH for about 5 minutes as described in P. 7, Note; the mass was extracted with water, and the residue treated with cold HCl (1.12): the rutile was not attacked by HNO_3 (P. 3) nor by HNO_3 and HCl (P. 4), but about 300 mg. Ti were dissolved by H_2SO_4 and HF (P. 5); much of the TiO_2 dissolved in the fused KOH, but only 2-3 mg. Ti passed into solution on treating the mass with water; out of the residue, which consisted of a black and white mixture, about 200 mg. Ti dissolved on treating with HCl (1.12): and a black residue of unattacked rutile still remained, which weighed 150 mg. corresponding to about 90 mg. Ti. This was powdered finely, again fused with KOH for 15 minutes, and extracted with dilute HCl: all but 3-4 mg. Ti dissolved.

Foreign Substances Introduced from Porcelain or Nickel Crucibles.—10 grams of a mixture of K_2CO_3 and Na_2CO_3 were fused in a porcelain crucible for half an hour over a powerful burner, the mass treated as described in the procedure, and

the residue and solution analyzed separately: the residue after the evaporation to dryness with HCl was shown by P. 5 to contain several milligrams of SiO_2; the solution was found to contain several milligrams of aluminum and of calcium and a trace of iron.

The experiment was repeated, using a nickel crucible: the aqueous extract acidified with HCl gave no precipitate with H_2S nor with NH_4OH and $(NH_4)_2S$. A slight black residue of a nickel oxide insoluble in water remained: this dissolved in HCl and gave a precipitate with NH_4OH and $(NH_4)_2S$, which was estimated to contain 1 mg. Ni.—This experiment was repeated, except that 0.3 mg. KNO_3 was added to the fusion: 4-5 mg. Ni as nickel oxide were obtained.

PART II. ANALYSIS OF THE SILVER, COPPER, AND TIN GROUPS

GENERAL DISCUSSION

A survey of the main features of the method adopted for the analysis of the hydrochloric acid and hydrogen sulphide precipitates may be obtained by referring to the "Tabular Outline" following this chapter. Here only the modifications introduced into the process ordinarily followed will be discussed.

In the precipitation and analysis of the silver group the usual process has been adhered to, the only addition being a provision for the detection of thallium by removing the lead with sulphuric acid and then adding potassium iodide.

In the direction for the precipitation of the copper and tin groups by hydrogen sulphide, especial attention is given to securing the proper conditions as to acid concentration and temperature for a satisfactory separation of these elements from those of the iron group; for indefiniteness in this respect is one of the most common sources of difficulty to the inexperienced analyst. In our process, as will be seen by reference to P. 21, it is directed to precipitate first from a hot, moderately acid solution. The fairly large acid concentration has the advantage of preventing the precipitation by hydrolysis of basic salts of titanium, bismuth and antimonous antimony, and of hastening the precipitation of the arsenic. The high temperature promotes the precipitation of arsenic, molybdenum, and platinum, and causes all the sulphides to separate in a more readily filterable form. The solution is, however, finally diluted so as to contain 4 cc. of hydrochloric acid of specific gravity 1.12 in 100 cc., and is saturated with hydrogen sulphide in the cold: for only with an acid as dilute as this and then in the cold is it possible to precipitate as little as 1 or 2 mg. of cadmium or lead. Attention may be called to our experiments described in the chapter on "Confirmatory Experiments and References," which show that under these conditions the separation is a remarkably satisfactory one—at any rate from a qualitative analysis point of view, since not