

3. OUTLINE OF THE ANNEXED ANALYTICAL TABLES.

HCl	H ₂ S	NH ₄ HS	(NH ₄) ₂ CO ₃	(NH ₄) ₂ HAsO ₄	
Hg (as mercurous salt)	Cd	Zn	Ba	Mg	K
Pb (partially)	Cu	Mn*	Sr		Na
	Hg (as mercuric salt)	Co	Ca		NH ₄
Ag	Pb (entirely)	Ni			
	Bi	Al			
	As (as arsenious or arsenic salt)	Fe			L
	Sb				
	Sn (as stannous or stannic salt)	Cr			
	Au				
	Pt				

The laboratory student should practise the examination of aqueous solutions of salts of the above metals until able to analyze with facility and accuracy.

GENERAL AND SPECIAL MEMORANDA RELATING TO THE PRECEDING ANALYTICAL TABLES.

General Memoranda.

These charts are constructed for the analysis of salts more or less soluble in water.—The student has still to learn how substances insoluble in water are to be brought into a state of solution; but, once dissolved, their analysis is effected by the same scheme as that just given. The Tables, especially the second (No. 2), may therefore be regarded as fairly representing the method by which metallic

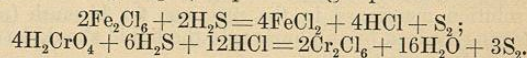
constituents of chemical substances are separated from each other and recognized.—The methods of isolation of the complementary constituent of the salt (the reactions of non-metals and acidulous radicals) will form the next object of practical study.

The general memoranda given in connection with the first Table (p. 219) are equally applicable to the extended second Table, and should again be carefully read through.

Special Memoranda.

The hydrochloric-acid precipitate may at first include some antimony and bismuth as oxychlorides, readily dissolved, however, by excess of acid.—If either of these elements be present, the washings of the precipitate will probably be milky; in that case add a few drops of hydrochloric acid, which will clear the liquid and make way for the application of the test for lead.

The sulphuretted-hydrogen precipitate may be white, in which case it is nothing but sulphur; for, as already indicated, ferric salts are reduced to ferrous, and chromates to the lower salts of chromium by sulphuretted hydrogen, sulphur being deposited:—



But the precipitate may also be colored, or even white when only lead or mercury is present, through an insufficiency of sulphuretted hydrogen having produced a peculiar oxysulphide or hydrato-sulphide. The gas should be passed through the liquid until, even after well shaking, it smells strongly of sulphuretted hydrogen.

The portion of the sulphuretted-hydrogen precipitate dissolved by sulphhydrate of ammonium may include a trace of copper, sulphide of copper being not altogether insoluble in sulphhydrate of ammonium.—On adding hydrochloric acid to the sulphhydrate-of-ammonium solution, a white precipitate of sulphur only may be produced, the sulphhydrate of ammonium nearly always containing free sulphur.—Strong hydrochloric acid does not readily dissolve small quantities of sulphide of antimony out of much sulphide of arsenicum; and, on the other hand, the strong hydrochloric acid takes into solution a small quantity of sulphide of arsenicum if much sulphide of antimony is present. The precipitate or the original solution should therefore be examined by the other (hydrogen) tests for these elements if doubt exists concerning the presence or absence of either. Tin remains in the hydrogen-bottle in the metallic state, deposited as a black powder on the zinc used in the experiment. The contents of the bottle are turned out into a dish, ebullition continued until evolution of hydrogen ceases, and the zinc is taken up by the excess of sulphuric acid employed; any tin is then filtered out, washed, dissolved in a few drops of hydrochloric acid, and the liquid tested for tin by the usual reagents.—Tin may be detected in the mixed sulphides of tin, arsenicum, and antimony by the blowpipe reaction (*vide Index*).

The portion of the sulphuretted-hydrogen precipitate not dissolved by the sulphhydrate of ammonium may leave a yellow semi-

fused globule of sulphur on boiling with nitric acid. This globule may be black, not only from presence of mercuric sulphide, but also from inclosed particles of other sulphides protected by the sulphur from the action of the acid. It may also contain sulphate of lead, produced by the action of nitric acid on sulphide of lead. In cases of doubt the mass must be removed from the liquid, boiled with nitric acid till dissolved, the solution evaporated to remove excess of acid, and the residue examined; but usually it may be disregarded.

—Before testing for bismuth, any considerable excess of acid should be removed by evaporation, and the residual liquid should be freely diluted. If no precipitate (oxynitrate of bismuth) appear, chloride-of-ammonium solution may be added, oxychloride of bismuth more readily forming than even oxynitrate.—Or any nitric acid or sulphuric acid having been neutralized by ammonia, hydrochloric acid is added, and then iodide of potassium; a rich orange color results if bismuth be present.—Bismuth may also be detected in the mixed precipitated hydrates of bismuth and lead, obtained in the ordinary course of analysis, by dissolving a portion of the precipitate in acetic acid and adding the liquid to the hot iodide of lead solution mentioned in the reactions for bismuth (p. 292).—In testing for lead by sulphuric acid the liquid should be diluted and set aside for some time.

Mercury may also be isolated by digesting the sulphuretted-hydrogen precipitate in sulphydrate of sodium instead of sulphydrate of ammonium. The sulphides of arsenicum, antimony, tin, and mercury are thus dissolved out. The mixture is then filtered, excess of hydrochloric acid added to it, and the precipitated sulphides collected on a filter, washed, and digested in sulphydrate of ammonium; sulphide of mercury remains insoluble, while the sulphides of arsenicum, antimony, and tin are dissolved. By this method copper also appears in its right place only, sulphide of copper being quite insoluble in sulphydrate of sodium. The other metals are then separated in the usual way.

The *sulphydrate-of-ammonium precipitate* may, if the original solution was acid, contain Phosphates, Oxalates, Silicates, and Borates of Barium, Calcium, and Magnesium. These will subsequently come out with the iron, and, being white, give the iron precipitate a light-colored appearance; their examination must be conducted separately, by a method described subsequently in connection with the treatment of substances insoluble in water.—The precipitates containing aluminium, iron, and chromium hydrates often contain some manganese. This manganese may be detected by washing the hydrates to remove all traces of chlorides, boiling with nitric acid, adding either puce-colored oxide of lead or red lead, and setting the vessel aside. If manganese be present a red or purple liquid is produced.—Sulphide of nickel is not easily removed by filtration (*vide* p. 234) until most of the excess of sulphydrate of ammonium has been dissipated by prolonged ebullition.

The *carbonate-of-ammonium precipitate* may not contain the whole of the barium, strontium, and calcium in the mixture, unless free ammonia be present; for the carbonates of those metals are

soluble in water charged with carbonic acid. If, therefore, the liquid is not distinctly ammoniacal, solution of ammonia should be added.—Neither carbonate nor hydrate of ammonium wholly precipitates magnesian salts; and, as a partial precipitation is undesirable, a solvent, in the form of an alkaline salt (chloride of ammonium), if not already in the liquid, should be added.—In the chart opposite p. 254 strontium is ordered to be separated from calcium by adding to the acetic solution diluted sulphuric acid. The latter, unless extremely dilute, may precipitate calcium. Any such loss of calcium is in itself of little consequence, because enough sulphate of calcium remains in the filtrate to afford a calcium reaction when ammonia and oxalate of ammonium are subsequently added. But the calcium precipitated by the sulphuric acid may be wrongly set down as strontium. Therefore test a little of the acetic solution for strontium by an aqueous solution of sulphate of calcium, when, if no precipitate falls after setting aside for several minutes, strontium may be regarded as absent. If a precipitate occurs strontium is present; the rest of the acetic solution is then tested for calcium as directed in the chart, the final testing by oxalate of ammonium being, of course, preceded by the addition of ammonia.

Lithium.—The search for lithium may usually be omitted. Should a precipitate, supposed to be due to lithium, be obtained, it must be tested in a flame (= scarlet tint), as a little magnesium not unfrequently shows itself under similar circumstances.

Spectral Analysis.—If present only in minute proportions, the lithium may also remain with the alkalies; it can then only be detected by physical analysis (by a prism) of the light emitted from a tinged flame—by, in short, an instrument termed a spectroscope. Such a method of examination is called spectral analysis, a subject of much interest and of no great difficulty, but scarcely within the range of Pharmaceutical Chemistry; it will be briefly described in connection with the methods of analyzing solid substances.

QUESTIONS AND EXERCISES.

404. Describe a general method of analysis by which the metal of a single salt in a solution could be quickly detected.
405. Give illustrations of black, white, light pink, yellow, and orange sulphides.
406. Mention the group-tests generally employed in analysis.
407. Under what circumstances may a hydrochloric precipitate contain antimony or bismuth?
408. If a sulphuretted-hydrogen precipitate is white, what substances are indicated?
409. Give processes for the qualitative analysis of liquids containing the following substances:—*a.* Arsenicum and Cadmium; *b.* Bismuth and Antimony; *c.* Ferrous and Ferric salts; *d.* Aluminium, Iron, and Chromium; *e.* Arsenicum, Antimony, and Tin; *f.* Lead and Strontium; *g.* Iron, Sodium, and Arsenicum; *h.* Mercury, Manganese, and Magnesium; *i.* Zinc, Manganese, Nickel, and Cobalt; *j.* Barium, Strontium, and Calcium.