REVIEW OF ANALYTICAL WORK DONE ABROAD IN 1904.

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A glance at the pages of the *Central-Blatt* will show that one could hardly quote all the titles of analytical papers published last year within the space limit of this review. The effort will be made to treat the reviewed articles generally with sufficient detail that the work may be repeated by an experienced analyst. For the general classification of subjects and for articles in journals, to the originals of which the writer has not access, he acknowledges his indebtedness to the above-mentioned journal.

GENERAL ANALYSIS.

Dittrich (*Ber.*, 37, 1840) published a scheme for the filtering and igniting of gelatinous precipitates (as ferric or aluminum hydroxide). It consisted in mixing with these, before filtering, a piece of filter-paper shaken to small pieces in water. The mixture will filter easily and give a fine powdery mass on ignition. L'Hote (*Ann. Chim. anal. appl.*, 9, 305) prepared sulphurous acid for use as a reagent and free from sulphuric by passing sulphur dioxide into a flask nearly full of boiling water, filling it then with boiling water and closing it immediately. Instead of a solution of gaseous hydrogen sulphide in water Sander (*Z. angew. Chem.*, 16, 202) used a solution of a sulphide, as sodium sulphide, which he decomposed with hydrochloric acid. Windisch (*Wochschr. f. Brauerei*, 21, 547) examined ten samples of market asbestos for filtering and found that they all contained matter soluble in water, some giving an alkaline reaction.

Optical.—Köthner (*Z. f. Naturw.*, 76, 81) discussed the problems of spectroscopic analysis for chemistry. The spectroscope is comparatively seldom used as an aid in qualitative analysis, chiefly because of the disturbing influence of spectra produced simultaneously and of complications caused by temperature and pressure. As examples of these influences he stated that a zinc cadmium alloy of nearly equi-molecular composition showed the zinc lines very weakly and a photogram of silver iodide showed no single iodine lines. Other uses of the spectroscope were discussed, as the testing of substances for impurities, the study of molecular processes and the determination of atomic weights. Nasini and Anderlini (*Atti R. Accad. dei Lincei Roma* [5], 13, I, 368; II, 59) have observed, contrary to the report of Palmieri, that at the temperature of the Bunsen flame helium could not be detected in certain volcanic incrustations from Vesuvius, also that neither the flame nor the electric spark will call forth the helium spectrum from uraninite, monazite, etc. The oxyhydrogen flame does not show the spectrum of hydrogen. In other words under ordinary conditions in flames the characteristic spectra of the gases are not obtained. They succeeded in obtaining a discontinuous emission spectrum for nitrogen at a much higher temperature, about 3000°. Experiments with iodine above 1000° were not successful, but they thought it was a question only of sufficient temperature. Matthes (*Z. anal. Chem.*, **43**, 73) used the Pulfrich immersion refractometer to determine the purity of many substances and the concentrations of solutions of sodium and potassium halides, acids, grape-sugar, cane-sugar, beer and wine extracts, etc., giving tables for these.

Combustion.—Collie (*J. Chem. Soc.* (London), **85**, 1111; *Proc. Chem. Soc.*, **20**, 174) described a method and the apparatus for the rapid combustion analysis of certain organic compounds. The carbon and hydrogen are determined by burning a known weight of the substance in a known volume of oxygen, the original method having been suggested by Saussure and Prout. The determination depends upon the measurement of gas volumes, hence is accurate; it can be applied only to substances not volatile in a vacuum. The apparatus is complicated, more so than the manipulation. Freiherr von Walther (*Pharm. Centr.-H.*, **45**, 489, 509) modified the filling of the tube for combustion analysis, using copper oxide-platinum asbestos and lead dioxide-silver asbestos for the carbon and hydrogen determination and powdered copper oxide for the nitrogen. He used also a special furnace.

Heating Value.—Alix and Bay (*C. R.*, **139**, 215) pointed out that nearly all coals contain more or less calcium carbonate, which is calculated in these determinations as carbon. The Mahler bomb was said by Arth (*Bull. Soc. Chim.* [3], **31**, 576) to be unsuited to the determination of the heating value of gases which contain only a small proportion of combustible gases. According to him the heating value can be calculated just as accurately and easily from a satisfactory analysis and then it is useless to make the bomb determination. Bazin (*Rev. gen. de Chim.*, **7**, 91) considered the practical steam-making capacity of a combustible material to be two-thirds of its found heating value (calorimetry or combustion). A comparative study of different types of calorimeters was made by Brame and Cowan (*J. Soc. Chem. Ind.*, **22**, 1230) and by Gray and Robertson (*Ibid.*, **23**, 704), and both agreed that reliable results can be obtained only with some form of bomb calorimeter. Gray and Robertson obtained under proper conditions fair results with the William Thompson instrument. Neither of these pairs of workers used the Parr calorimeter, but Mohr (*Wochschr. f. Brauerei*, **21**, 54) did and he decided that it is not yet technically usable. The bomb calorimeter was favored by him also.

Gas.—The separation of methane and hydrogen by fractional combustion caused by heated palladium wire was said by Richardt (*J. f. Gasbel.*, **47**, 566, 590) to work all right under proper conditions. The wire must not glow and the contact of gas with the wire must be neither too long nor too short. Ethane behaves like methane with regard to hydrogen, but it cannot be separated from methane by this means. Neither can ethylene. Macri (*L'Industria chimica*, **6**, 285) stated that the Clemens Winkler method of fractional combustion over palladium asbestos for the separation of hydrogen and methane is not satisfactory for separation, but may be used for the determination of both together. Morelli and Colonna (*L'Industria chimica*, **6**, 61) have modified the Orsat-Lunge apparatus so as to work with small amounts of gas in the presence of mercury, and to be able to carry out the combustion of explosive mixtures without danger. Sodeau (*Chem. News*, **89**, 61) also modified the Orsat apparatus, putting in place of the cuprous chloride pipette a Winkler combustion pipette to which is attached its own level bottle. The carbon monoxide and hydrogen are then determined by combustion. St. Martin (*C. R.*, **139**, 46) determined carbon monoxide in the air by shaking thirty minutes with fresh dog's blood so diluted as to contain about 0.15 per cent. of haemoglobin, and examining spectro-photometrically and reading off the content of carbon monoxide in air from tables. Wohl (*Ber.*, **37**, 433) has extended his method of gas analysis by measurement of pressures to the determination of heavy hydrocarbons and to combustion analysis. In another article (*Ibid.*, **37**, 429) he pointed out an error in the calculation of results of combustion analyses of gases. Avogadro's rule must be considered to hold good for the relations between hydrogen, oxygen, carbon monoxide and methane for the errors do not exceed 0.2 per cent. But with carbon dioxide this is not so; the difference in molecular volume compared to carbon monoxide is 0.6 per cent. and to methane 0.8 per cent. Besides the main contraction demanded by Avogadro's rule there is in burning carbon monoxide a further contraction of 0.6 per cent. of the carbon dioxide volume present, so that in calculating carbon monoxide one would find 1.2 per cent. too much. His formulae for the calculation of hydrogen, carbon monoxide and methane are: $H = K - O - 0.006\ CO_2$; $CO = {}^1/_3K - O + {}^3/_4CO_2 + 0.006\ CO_2$; $CH_4 = -{}^1/_3\ K + O - {}^1/_3CO_2$ (K = contraction, O = oxygen used and CO_2 = carbon dioxide formed).

Soil and Fodder.—Edwards (*Chem. News*, **89**, 183) described a rapid method for the analysis of soils, intended chiefly for analytical chemists at manure works. The determinations include water, organic matter, phosphoric acid, iron oxide and alumina, lime, potash and nitrogen. Hall (*Proc. Chem. Soc.*, (London) **20**, 152; *J. Chem. Soc.*, **85**, 950) discussed the mechanical analysis of soils by the Osborne settling method with and without previous treatment with dilute acid and ammonia. His results show that it is better to treat with acid and ammonia before subjecting the material to the fractional settling. Hazard (*Chem. Ztg.*, **28**, 210) gave a shortened method for the determination of potash in soils, potash residues, etc. He evaporated the acid soil solution in a porcelain dish, extracted the residue with water in platinum, precipitated with ammonia and ammonium carbonate, heated the precipitate to dryness and ignited to drive off the ammonium salts and burn up organic matter. He then extracted the residue with hot water and determined potassium in the filtrate with chlorplatinic or perchloric acid. A method for the volumetric determination of the humus content of the soil by means of permanganate solution was proposed by Istscherekow (*J. f. exp. Landw.*, **5**, 55). He boiled the crushed soil for forty or fifty minutes with permanganate solution, and titrated the excess with oxalic acid, or to dissolve the dioxide formed, added excess of oxalic acid and titrated with permanganate.

Duschetschkin (*J. russ. phys.-chem. Ges.*, **36**, 71) prepared crude fiber from fiber containing vegetable lignin by heating for from one and one-half to six hours (according to lignin content) with two parts of sodium peroxide and six parts of magnesium sulphate to one part of substance, with preliminary treatment of substance with 1 per cent. sodium hydroxide solution if lignin content be large. Lührs (*Chem. Ztg.*, **28**, 357) determined the sand content of a commercial fodder by heating it in a Kjeldahl apparatus for about half an hour with concentrated sulphuric acid, adding an oxidizing agent till the solution cleared, cooling, diluting with water, decanting from the sand, washing and weighing this in platinum. Mayer (*Chem. Ztg.*, **28**, 406) considered Lührs' method too involved and extracted the fodder with chloroform in a short-tubed separatory funnel, then allowed the sand settlings to run into a platinum dish and ignited.

Water.—Drawe, Procter, Auerbach and Basch (*Chem. Ztg.*, **27**, 1219, 1277; **28**, 16, 31) had each a different explanation for the occasional residual alkalinity of a hard water after long boiling. Pfeifer had ascribed this alkalinity to magnesium carbonate which is not insoluble in water. Drawe claimed a soda content for every natural water, which Procter said could not be as long as the water showed a permanent hardness. Procter apparently favored Pfeifer's explanation. Auerbach maintained that the small amounts of carbonate in solution are completely dissociated any way, so that it makes no difference whether one considers the alkalinity due to sodium carbonate or to calcium or magnesium carbonate; he favored soda. Basch stated that soda in solution is to be regarded as sodium hydroxide and primary sodium carbonate; he said Pfeifer's statement that soda reacts not at all or only very slightly with phenolphthalein is not true. Soltsien (*Pharm. Ztg.*, **49**, 218) added to this argument that the evaporation residues of waters ordinarily react alkaline, often strongly so, and that this is due in most cases to magnesium carbonate because sodium carbonate is found in ordinary waters, if at all, only in traces. Legler (*Pharm. Centr.-H.*, **45**, 585) gave a new method for the determination of the degree of hardness of a water. He evaporated the water sample to dryness with excess of hydrochloric acid, or if it was hard, boiled it with excess of tenth-normal hydrochloric acid till all the carbon dioxide was gone, and then neutralized with tenth-normal alkali in presence of aqueous methyl orange. The neutral water, or water residue dissolved in water, was then treated with an excess of a definite mixture of potassium oxalate and sodium hydroxide, boiled, made up to a definite volume, and one part of the clear filtrate used for the determination of calcium, the other for magnesium. For this purpose one part of the filtrate was treated with excess of tenth-normal sulphuric or hydrochloric acids and neutralized in presence of rosolic acid or of phenolphthalein, while the other portion was acidified, warmed and titrated with permanganate. Buttenberg (*Gesundh.-Ing.*, **26**, No. 15) found that distilled water would attack lead strongly. Lenormand (*Bull. Soc. Chim.* [3], **31**, 139) showed that a salt or sweet water solution will take up organic matter from filter-paper so that it is inadvisable to filter waters before analysis. Lohmann (*Z. öffentl. Chem.*, **9**, 458) distinguished between distilled and ordinary water in artificial mineral waters by their optical behavior; a layer 50–75 cm. thick will appear greenish blue if distilled water is used, whereas it will appear brownish with ordinary water. The silica test recommended by Silber the author stated to be of no value, because silica ought to be added to give the water a mineral-like taste.

Electroanalysis.—Brochet and Petit (*C. R.*, **138**, 359, 419) gave some experiments with different metals and different electrolytes using the alternating current, and opposed LeBlanc's view that the solution of copper in potassium cyanide solution is caused by the formation of complex ions under the influence of the current. There are three classes of cases where no formation of complex ions takes place, according to these authors. They are (1) stable electrolytes (with evolution of oxyhydrogen gas), (2) solution of the electrodes, and (3) oxidation or reduction. Examples were given. Pearce and Couchet (*Ibid.*, **138**, 361) observed that reduction of higher stages of oxidation by means of the alternating current depends upon the nature of the electrodes as well as upon current density and number of alternations. With small current density only solution of the electrodes is observed. The reduction of ferric alum is slight with platinum, greater with aluminum, lead or cadmium, and nearly quantitative with iron electrodes. Haber and Schwenke (*Z. Elektrochem*, **10**, 143) devised an electrochemical method for determining the amount of attack on glass, especially bottle-glass, by water. Water which would conduct was placed in the bottles and then they were heated for five hours at 80°. Electrodes were introduced through the neck and the conductivity measured every hour. The current strength corresponding to 30, 20 and 10 volts tension was determined with an ammeter and the resistance calculated graphically. The conductivity of the water minus the initial conductivity divided by the time of action gives for every glass its rapidity of solution, a value nearly constant for each glass, and characteristic. Some of the brown and green wine-bottles were nearly as little attacked as Jena glass.

Volumetric.—Kühling (*Chem. Ztg.*, **28**, 596, 612) and Lunge (*Ibid.*, **28**, 701) had a portion of their discussion over the suitability of potassium tetroxalate as a standard titration substance. The discussion was begun in 1903, Kühling maintaining that the tetroxalate prepared according to his directions was satisfactory, while Lunge insisted that it would not yield as good results as would soda or Sorenson's sodium oxalate. Raschig (*Z. angew. Chem.*, **17**, 577) recommended as original titration substances crystallized oxalic acid and sodium carbonate, also a water solution of gaseous hydrochloric acid, and further sulphur dioxide solution for iodometric titrations. Raschig's method of standardizing the gaseous hydrochloric acid solution was described by Moody in 1898, according to Lunge (*Ibid.*, **17**, 886). Lehfeldt (*Pharm. Ztg.*, **49**, 146) recommended potassium biiodate for iodometry, sublimed oxalic acid (Merck) for acidimetry, and the preparation of hundredth-normal solutions of hydrochloric acid and caustic potash by titration against oxalic acid in the presence of iodeosin. Cantoni and Basadonna (*Ann. Chim. anal. appl.*, **9**, 365) criticized the ordinary methods of standardization of permanganate with iron wire, Mohr's salt and oxalic acid, and recommended the iodometric method of Volhard. Dupré (*Z. angew. Chem.*, **17**, 815) likewise recommended the Volhard method, preferring it to the electrolytic because of its simplicity. Skrabal (*Z. anal. Chem.*, **42**, 741) had the end of his argument with Classen regarding "Classen electrolytic iron." Skrabal maintained that it was impure. In another article (*Ibid.*, **43**, 97) he gave a couple of methods for preparing ferrous ammonium sulphate from which he obtained iron by the Classen method, but after it was precipitated it was carried by means of a weak current from one electrode to the other. Gardner and North (*J. Soc. Chem. Ind.*, **23**, 599) found that pure permanganate in pure water would preserve its original strength for at least twelve months. Ammonium oxalate deteriorated at the rate of about 1 per cent. a fortnight for seven months. Potassium bromide was recommended by Berti (*Bull. de l'Assoc. d. Chim. de Sucr. et Dist.*, **21**, 1234) and sodium sulphide by Beulaygue (*C. R.*, **138**, 51) as indicators for the determination of sugars by means of Fehling's solution. A violet color, due to the formation of water-free cuprous (?) bromide, indicates that there is still copper in solution when a very small amount of solution is brought into contact with a small crystal of potassium bromide on porcelain and then concentrated sulphuric acid added. A yellow color, due to free bromine, is obtained when the copper is all out of solution. If a double layer of filter-paper be touched with the Fehling's solution and the untouched one of the two paper layers then touched in the moistened spot with freshly prepared 10 per cent. sodium sulphide solution, the paper will show dark by transmitted light at the touched spot as long as copper is present in solution. Robin (*Ann. Chim. anal. appl.*, 9, 130; *C. R.*, **138,** 1046) prepared a new indicator by heating the yellow mimosa blossoms in 200 cc. of water to beginning boiling and after cooling adding 50 cc. of neutral 95 per cent. alcohol, allowing to settle and filtering into a brown bottle. It gives an intensely yellow color with alkalies and is colorless in acid solutions. On evaporation of some of the indicator with material containing boric acid, the residue is yellow and becomes red with a few drops of soda solution. Without boric acid the indicator residue would be gray and yellow under these two conditions. Scholtz (*Z. f. Elektrochem.*, **10**, 549) determined the strength of indicators as bases or acids by titrating an acid solution with a base, like caustic potash, when the stronger acid indicator will change color first (as *p*-nitrophenol before phenolphthalein). If basic indicators are mixed with the acid the order in which they change color in the above titration is weakest base, strongest base, strongest acid, weakest acid. The following is the order found by the author, beginning with the strongest acid: (1) alizarinsulphonic acid, iodeosin; (2) *p*-nitrophenol; (3) luteol; (4) haematoxylin, rosolic acid; (5) litmus; (6) turmeric; (7) phenolphthalein. Of those with less sharp color changes, cochineal is stronger than litmus, alizarin lies between *p*-nitrophenol and litmus, and fluorescein between iodeosin and litmus. Cyanine is a stronger basic indicator than methyl orange or the tropaeolins. Rosenthaler (*Arch. der Pharm.*, **241**, 589) described the spontaneous change which takes place in Fehling's solution.

Microchemical.—Behrens (*Z. anal. Chem.*, **43**, 333) gave a goodly number of microchemical reactions for the detection of different classes of organic bases as the anilines, aminophenols, benzylamines, diamines, pyridines, various alkaloids, etc. Paraffin oil was recommended by Harz (*Z. f. wiss. Mikrosk.*, **20**, 179; **21**, 25) as a substitute for Canada balsam for permanent microscopical preparations, and a solution of 1 part of iodine in 100 parts of gently warmed paraffin oil as an imbedding medium. Wieler (*Chem. Ztg.*, **28**, 1014) pointed out a structure resembling cell structure in basic precipitates, especially basic copper carbonate, and said that such structure might be looked for in natural precipitates such as minerals, and succeeded in showing a honeycomb-like structure in malachite, dolomite and carbonate of nickel.

ANALYSIS OF ORGANIC COMPOUNDS.

Gasparini (*Atti R. Accad. dei Lincei Roma* [5], **13**, II, 94) gave a new method for the destruction of organic matter in toxicological analysis. He electrolyzed the nitric acid solution, using a current of 4 to 6 amperes and 8 volts. The oxidation was sometimes complete in a few hours and sometimes required days. Some metals (copper, lead, silver, etc.) colored the solutions near the electrodes or gave precipitates. Tin and antimony were precipitated as higher oxides, while arsenic remained in solution as arsenic acid. Monthulé (*Ann. Chim. anal. appl.*, **9**, 308) destroyed organic matter for the determination of phosphorus and arsenic as follows: he saturated the substance in a porcelain crucible with a solution of magnesium oxide in nitric acid (sp. gr. 1.38) of which 100 cc. contained 10 grams of magnesia. This mixture he evaporated as far as possible on the water-bath, then on a sand-bath and finally ignited over a free flame at low redness. If a carbonaceous residue remained, he added nitric acid, dried and ignited again. He then dissolved the residue and treated the solution with magnesia mixture. Von Konek (*Z. angew. Chem.*, **17**, 771, 886, 888, and 1093 (with Zöhls)) described the use of sodium peroxide in organic analysis, both qualitative and quantitative. By its use all the ordinary elements except hydrogen and oxygen may be detected. The author used a thick-walled nickel or steel cylindrical crucible of about 2 cm. diameter and provided with a screw cover which had a hole in the middle, and into which a nickel or steel tube 10 cm. long and 1 to 2 mm. inside diameter fitted. Five to 10 grams of dry sodium peroxide were placed in the crucible, a good knife point full of the substance added, the mixture stirred, the cover screwed on, the crucible placed in a dish of cold water and the hot wire for ignition thrown in through the metal tube. The combustion is explosive. Carbon is oxidized to carbon dioxide, nitrogen and phosphorus to the pentoxides, the halogens to the halides, sulphur to sulphur trioxide, and arsenic, selenium, tellurium, boron and antimony to arsenic, selenic, telluric, boric and antimonic acids, the heavy metals remaining as oxides or hydroxides. Some quantitative methods, especially an indirect one for carbon, were given. Von Konek criticized also the form of crucible recommended for a similar use by Pringsheim, who replied to this *Ibid.*, **17**, 1454). Pringsheim (*Ber.*, **37**, 2155) also published an article along lines similar to the above. Herzog (*Z. f. Farben- und Textilchemie*, **3**, 259) showed that natural and artificial silk may be distinguished from each other by their behavior toward polarized light; artificial silk shows dichroism, natural does not.

Alcohols and Acids.—Gnehm and Kaufler (*Z. angew. Chem.*, **17**, 673) proposed a new method for the determination of methyl alcohol in formaldehyde. The latter compound forms a condensation product with sodium sulphanilate, and the methyl alcohol may then be driven off by distillation. They determined the alcohol from the density of the distillate, but Bamberger (*Ibid.*, **17**, 1246) said that the old method of distilling the alcohol after condensation with primary sodium sulphite gives better results. Kling and Viard (*C. R.*, **138**, 1172; *Bull. Soc. Chim.*, (3), **31**, 783) gave a method for distinguishing the primary, secondary and tertiary alcohols of the fatty series. Tertiary alcohols decompose into unsaturated hydrocarbons at or below the boiling-point of naphthalene, secondary alcohols do not decompose before the boiling-point of anthracene is reached, while primary ones remain undecomposed at this temperature. Then a V. Meyer vapor-density determination first in naphthalene vapor, then in anthracene vapor, will show whether the alcohol is a primary, secondary or tertiary one. Ley (*Pharm. Ztg.*, **49**, 149) proposed the following method for the determination of tartaric acid. He heated the water or alcohol solution of tartaric acid, treated it with alcoholic zinc acetate solution, heated again, then added 100–150 cc. of alcohol and 5 cc. of 50 per cent. acetic acid. The whole was then heated on the water-bath, filtered by suction, washed and ignited. Dubosc (*Ann. Chim. anal. appl.*, **9**, 45) proposed to determine sulphocyanates in the presence of salts which give precipitates with silver nitrate by oxidizing the sulphur of the sulphocyanate to sulphate. He used the chlorine liquor (18–20 grams of active chlorine per liter) obtained from the electrolysis of chlorides for this oxidation. In 50 cc. of water he took enough of the sulphocyanate to yield probably 0.2 to 0.4 gram of barium sulphate, added to the solution 2 grams of barium chloride dissolved in 50 cc. of water and then gradually 50 cc. of the electrolytic liquid. This was allowed to stand some ten minutes, was then acidified with hydrochloric acid, boiled and filtered. A method for the volumetric determination of hydrocyanic acid in cyanides was given by McDowall (*Chem. News*, **89**, 229). He used an ammoniacal copper sulphate solution. The passage to colorless is sharp and the presence of chlorine is without influence.

Carbohydrates.—Benz (*Z. f. Unters. Nahr.-Genussm.*, **7**, 84) suggested that the hour digestion or half-hour shaking of the accepted method for the determination of soluble carbohydrates in food material be changed to twenty-four-hour digestion, because in one hour not all of the actually soluble carbohydrates go into solution. Goodwin and Tollens (*Ber.*, **37**, 315) dried furfurolphloroglucide at 103° in a current of hydrogen to avoid oxidation and found that its formula is $C_{11}H_8O_4$, not $C_{11}H_6O_3$. Two new methods of sugar determination were proposed by Oerum (*Z. anal. Chem.*, **43**, 356). In one the cuprous oxide precipitated as usual was separated from the liquid by means of an asbestos filter, dissolved in nitric acid and the copper determined by the use of Meisling's universal colorimeter. The other was a modification of the Sachsse mercury method. A solution of 18 grams of pure dry mercuric iodide, 25 grams of potassium iodide and 80 grams of caustic potash was made and diluted to one liter with water. Of this solution 20 cc. were boiled in a small flask with 80 cc. of water, then 5 cc. of urine so diluted as to contain not more than 1.3 per cent. of sugar were added and the boiling continued for a few minutes. The precipitated mercury was filtered through a good filter, washed with hot 1 per cent. hydrochloric acid, then with water and dissolved in nitric acid. The solution was diluted and the mercury determined by the Volhard method, using ammonium ferric alum for indicator. Another sugar determination was given by Rosenthaler (*Z. anal. Chem.*, **43**, 252). When sugars are oxidized by alkaline copper solution acids are formed and these neutralize a portion of the alkali in the solution. If a portion of the alkaline copper solution alone be titrated with normal acid and then a similar portion after the sugar treatment, the difference between the two figures will give the amount of alkali neutralized by the acids from the sugar. In practice Rosenthaler added excess of normal acid and titrated back with normal alkali, using phenolphthalein for indicator. Riegler (*Bull. Soc. des Sciences de Bucarest*, **13**, 20) gave a rapid gasometric method for the determination of sugar in urine. The sugar was oxidized by boiling the diluted liquid with a little potassium permanganate, adding the liquid to more permanganate, cooling, evolving by means of sulphuric acid and measuring the carbon dioxide from the carbonate formed. $C_6H_{12}O_6 + 8KMnO_4 = 4K_2CO_3 + 2CO_2 + 8MnO_2 + 6H_2O$. Pflüger (*Pflüger's Arch.*, **103**, 169) gave a shortened method of determining glycogen. He heated 100 grams of fresh material for two hours in 100 cc. of 60 per cent. potassium hydroxide. On cooling, 200 cc. of water were added and 400 cc. of 96 per cent. alcohol. After filtration the precipitate was washed once with a mixture of one volume of 15 per cent. caustic potash and two of 96 per cent. alcohol, then with 66 per cent. alcohol and finally dissolved in boiling water. He neutralized the solution, removed the albumen precipitated, neutralized again and then added hydrochloric acid to a concentration of 2.2 per cent. The inversion required three hours. The solution was then cooled, neutralized, filtered and the sugar determined. The sugar value was multiplied by 0.927 for the glycogen value. Cellulose may be determined in food products, etc., by a modification of this Pflüger glycogen method, according to Simon and Lohrisch (*Z. physiol. Chem.*, **42**, 55). They heated 10 grams of the substance for one hour on the water-bath with 50 per cent. caustic potash, and on cooling added 3 to 4 cc. of hydrogen peroxide. The material all dissolved, at least if treatment with peroxide were repeated. On addition of one-half volume of 96 per cent. alcohol the cellulose was precipitated. It was filtered by suction on to a hardened filter, washed with water and weighed.

Alkaloids.—Kley (*Z. anal. Chem.*, **43**, 160) found that the alkaloids might be very well distinguished by measuring roughly their indices of refraction. Small crystals were placed in a series of solutions of varying but known indices of refraction, placed between two nicols, and the comparison carried on till the index of the crystal and of the liquid were the same. Among the large number of analytical articles dealing with the characteristics of alkaloids, attention will be called here only to two by Leger (*J. Pharm. Chim.* (6), **19**, 329, 479) and to nine by Reichard (*Chem. Ztg.*, **28**, 299, 339, 912, 977, 1048, 1102; *Pharm. Ztg.*, **49**, 523, 855; *Pharm. Centr.-H.*, **45**, 645). Leger gave the results of investigations upon the root bark of the pomegranate, upon coca, belladonna, nux vomica, *fabae ignatii*, ipecac and Peruvian bark. Reichard's investigations covered the reactions of morphine, cocaine, atropine, strychnine, brucine and antipyrine. Wörner (*Pharm. Ztg.*, 49, 628) stated that Reichard's new test for morphine with formaldoxime and sulphuric acid is practically the known Marquis test with formaldehyde and sulphuric acid.

Coloring Materials and Tannins.—Lambrecht and Weil (*Ber.*, **37**, 303) gave a quick method for distinguishing between rosaniline and pararosaniline. The former dissolves completely in twenty volumes of 30 per cent. hydrochloric acid on warming and yields no precipitate when this solution stands, while pararosaniline forms with the same amount of acid difficultly soluble hydrochlorides which crystallize out on cooling nearly completely. The addition of 0.5 per cent. of pararosaniline can be detected on twelve hours' standing by the brown crystals. Riegler (*Z. anal. Chem.*, **43**, 539) used an alkaline alcoholic hydrazine solution as a test for blood. His reagent he prepared by dissolving 10 grams of sodium hydroxide in 100 cc. of water, adding 5 grams of hydrazine sulphate, 100 cc. of 96–97 per cent. alcohol, and filtering after two hours. Blood shaken with this solution and allowed to stand gives a magnificent purple-red solution of haemochromogen. Shaken vigorously in the air the solution turns greenish and shows the absorption spectrum of haematin (one band). On standing, the solution turns red again, showing then the absorption of haemochromogen (two bands, similar to those of the original blood solution, but moved a little toward the violet).. Parker and Payne (*J. Soc. Chem. Ind.*, **23**, 648) proposed a new method for the determination of tannins which rests on the fact that digallic acid forms, with excess of lime, a basic salt insoluble in water. $C_{14}H_{10}O_9 + 4Ca(OH)_2 = C_{14}H_{10}O_9Ca_4(OH)_8$. Bogh (*Collegium*, 1904, p. 301) called attention to the fact that the equivalent used by Parker and Payne (40 liters of fifth-normal calcium hydroxide to 322 grams of tannin) is all right for the tannins of the pyrogallol series, but that for the catechol series it must be multiplied by $^3/_2$. With old tannin material the method gives results which do not agree with those obtained by the gravimetric method. Dreaper (*Chem. News*, **90**, 111), in view of the above-mentioned method, called attention to his own method of precipitation by means of calcium or barium salts and subsequent titration with copper sulphate, published in 1893.

Parker and Payne said that their method gives results agreeing with those of the common method, but Dreaper showed in 1893 that the latter would give values for tannic acid in a substance certainly free from it, and hence was analytically worthless. Dufour (*Collegium*, 1904, p. 337. Extract from *La Conceria*) showed that the caramel obtained from starch, sugar, etc., which gives none of the reactions characteristic of tannin, is more or less completely absorbed with the tannin in the official analysis. Wislicenus (*Z. angew. Chem.*, **17**, 801) found that aluminum hydroxide may be used as the precipitating agent for the tannins instead of powdered hide.

Ethereal Oils and Wine.—Fendler (*Ber. d. pharm. Ges.*, **14**, 208) gave a method of determining water, insoluble matter, pure rubber and resin in crude rubber practically in one operation. The water was determined by simply drying over sulphuric acid. The insoluble impurities were obtained by treating 2 grams of the finely divided sample in a 100 cc. measuring flask with petroleum ether till nothing more would go into solution, then adding petroleum ether to 100 cc. and allowing to settle. The mixture was then filtered through a layer of glass wool in an Allihn tube, 50 cc. into a 50 cc. flask, the rest into another vessel. The residue on the glass wool, washed with the solvent, dried and weighed, gave the insoluble impurities in 2 grams of crude rubber. The pure rubber in 1 gram of crude was determined in the first filtered 50 cc. by shaking with about 70 cc. of absolute alcohol in a weighed 200 cc. flask, pouring off the petroleum ether-alcohol mixture, washing the usually balled mass of pure rubber with alcohol, drying in a water-drying oven with a blast of air and weighing flask and contents. The resin in 1 gram of the crude rubber was determined by distilling the petroleum ether-alcohol mixture and the alcohol washings mentioned above from a weighed flask, and drying and weighing the residue. In another article (*Ibid.*, p. 215) Fendler compared three of the newer methods for rubber analysis. They were that of Harries (*Ber.*, **34**, 2991; **35**, 3256, 4429; **36**, 1937), of Weber (*Ibid.*, **35**, 1947; **36**, 3103) and his own just described. He found that the methods of Harries and Weber gave like results for pure rubber in crude, and that both were in many cases too high; that Harries' method was preferable to Weber's because of its greater simplicity; that the values for insoluble constituents obtained by either method were wide of the mark, and that his own method gave usable results in the analysis of crude rubber and was of value because of its simplicity. Raikow and Schtarbanow (*Chem. Ztg.*, **28**, 886) observed that it was possible to obtain a measure of the volatile constituents besides alcohol in wine by comparing the alcohol content found by determination of the flashing-point of the wine (which result is always too high) and by distillation. Spica (*Gaz. chim. ital.*, **33**, II, 482) detected salicylic acid in wine by converting it into picric acid and coloring wool yellow with it. If the yellow color were not due to picric acid or to salicylic acid, it would not color wool a second time, if the color were removed by alkali, the liquid made acid and fresh wool dipped in it. The first coloration would be proof of salicylic acid, if the original extraction were made with carbon disulphide instead of ether.

Milk, Blood and Fats.—Ertel (*Milch-Ztg.*, **33**, 81) took exception to some of the statements of Ripper concerning milk. Ripper stated that the index of refraction of the milk serum was a criterion as to whether the milk came from a sound or a sick cow, the normal being 1.3430-1.3442 while that of milk serum from sick cows is 1.3410-1.3427. Ertel showed that this index of refraction for the milk of sound cows does not vary much and yet often exceeds the limits given by Ripper, going more often above than below, and also that that of sick cows' milk often runs above 1.3440. It varies more with sick than with well animals and will vary with the same animal. Salaskin and Pupkin (*Z. physiol. Chem.*, **42**, 195) used the Salkowski principle (titration of the ammonia driven out of ammonium salts by blood) to determine the alkalinity of blood, but Folin (*Ibid.*, **43**, 18) stated that ammonia added to blood can not be completely driven out at any temperature. Toward the end of 1903 Partheil and Ferié (*Arch. der Pharm.*, **241**, 545) published a separation of the saturated fatty acids depending in large measure upon the solubilities of the lithium salts, and they obtained some very good results. But Farnsteiner (*Z. f. Unters. Nahr.-Genussm.*, **8**, 129) and Fahrion (*Z. angew. Chem.*, **17**, 1482) both unconditionally condemned the method. Heermann (*Chem. Ztg.*, **28**, 53, 60, 702) criticized most of the usual methods for the determination of small amounts of sodium carbonate and hydroxide in soaps and gave an improvement on his modification of the salting-out method. The first two articles were the signal for a polemic with Schmatolla (*Ibid.*, **212**, 611, 711), in which Berg (*Ibid.*, **212**, 691) joined, upon the alkalinity and the dissociation of soaps. Heermann determined the sodium hydroxide by precipitating the fatty and carbonic acids with barium chloride, then titrating the liquid with standard acid, using phenolphthalein as indicator. For the sodium carbonate, he salted out with sodium chloride and titrated directly with methyl orange as indicator, and then subtracted the value found for sodium hydroxide; or he dissolved the soap in absolute alcohol, saturated the sodium hydroxide with carbon dioxide, filtered, washed with cold absolute alcohol, dissolved the precipitate in hot water and titrated with methyl orange as indicator. Schmatolla stated that soaps can split in two ways and endeavored to show why Heermann's determination of free alkali in soaps was unreliable. Heermann replied. Berg also opposed some of Schmatolla's conclusions.

ANALYSIS OF INORGANIC COMPOUNDS.

Metalloids.—The conditions under which it is possible to get an accurate determination of hydrogen peroxide in the presence of potassium persulphate by means of potassium permanganate were given in detail by Friend (*Proc. Chem. Soc.*, **20**, 65, 198; *J. Chem. Soc.*, **85**, 597, 1533). He concluded that the reason for the unsatisfactoriness of the determination under ordinary conditions is the slow interaction of peroxide and persulphate thus: $H_2O_2 + K_2S_2O_8 = K_2SO_4 + H_2SO_4 + O_2$. A colorimetric determination of hydrogen peroxide was devised by Planès (*J. Pharm. Chim.* (6), **20**, 538) depending upon the liberation of a molecule of iodine from potassium iodide by a molecule of peroxide in the presence of dilute sulphuric acid, the color of this iodine solution being compared with that of tenth-normal iodine solution.

To determine the purity of commercial sulphur Ceruti (*Boll. Chim. Farm.*, **43**, 421) dissolved the sulphur of the product in aniline of boiling-point 180–185°, precipitated it with acid and weighed it. Feld (*Z. anal. Chem.*, **42**, 708) gave two methods for the determination of sulphide and chloride together. One is to distil the hydrogen sulphide off with magnesium sulphate in a current of carbon dioxide, receive it in an iodine solution of known strength and then to precipitate the halide in the regular manner with silver nitrate. In the other, both are precipitated with excess of silver salt, the whole made up to definite volume and the excess of silver determined in one portion of the liquid by titration with ammonium sulphocyanate. The precipitate and the rest of the liquid are distilled in a current of carbon dioxide with aluminum turnings and hydrochloric acid, when the conversion of silver sulphide into silver and hydrogen sulphide goes smoothly; the hydrogen sulphide may be determined as in the other method with iodine solution. Total sulphur, when sulphur is present in forms other than sulphide, may be determined by a slight modification of this latter method. Sulphur was determined in calcium carbide by Lidholm (*Z. angew. Chem.*, **17**, 558) by fusing the material over an alcohol flame with five parts of potassium and sodium carbonates and two of ammonium chloride. The melt and crucible were put into a flask and distillation carried on with water and hydrochloric acid in a current of carbon dioxide. The hydrogen sulphide was led into two absorption flasks containing cadmium and zinc acetates and acetic acid, then the sulphides were converted into copper sulphide and ignited to copper oxide. Orloff (*J. russ. phys.-chem. Ges.*, **36**, 1311) proposed a method for the determination of hydrosulphurous acid and one for formalin also.

$$HgI_2.2KI + Na_2S_2O_4 + 4NaOH = Hg + 2NaI + 2KI + 2Na_2SO_3 + 2H_2O$$
$$Hg + I_2 = HgI_2.$$

Ten cc. of the double salt solution (60 grams mercuric chloride and 260 grams potassium iodide in one liter) were mixed with a potassium hydroxide solution and the solution of the material to be investigated. The mercury was filtered, washed, put into a solution of sodium hydroxide, then excess of tenth-normal iodine solution was added and, after acidification, titrated back with tenth-normal thiosulphate. The formalin method was similar. $HgI_2.2KI + 3KOH + HCOH = Hg + 2KI + HCOOK + 2H_2O$. Pozzi-Escot (*Rev. gen. de Chim.*, **7**, 240) proposed to determine sulphur in easily volatile organic compounds by oxidation with chromyl chloride. He put 1 gram of substance into a 500 cc. flask with 10 to 15 grams of pure dry chromium trioxide and 20 to 25 cc. of hydrochloric acid as pure and as concentrated as possible, then let it stand for thirty minutes and heated to boiling with a return-flow condenser for ten. With excess of chromium trioxide the oxidation is complete. The chromium was reduced with alcohol and the sulphuric acid determined with barium chloride. A new method for the determination of sulphur in iron and steel was proposed by Polsifer (*Chem. News*, **90**, 230), who dissolved the sample in chloric acid, a very little hydrofluoric and lastly hydrochloric acid and filtered the residue, which he then rendered soluble in water and hydrochloric acid by fusion with sodium peroxide. The two solutions were put together and the sulphuric acid precipitated with barium salt. Rossi (*L'Industria chimica*, **6**, 253) determined the amount of sulphuric acid in commercial acetic acid by making use of the fact that the latter is indifferent to methyl orange in alcoholic, formaldehyde or especially acetone solution, so that the sulphuric acid may be titrated with sodium hydroxide in one of these solutions.

Gutbier (*Z. anorg. Chem.*, **41**, 448) found that from compounds in which selenium or tellurium had a valence of 6 the element was not completely precipitated by phosphorous acid, but that from compounds of lower valence the reduction was rapid. Gallo (*Atti R. Accad. dei Lincei Roma* [5], **13**, I, 713; *Gaz. chim. ital.*, **34**, II, 404) electrolyzed tellurium from a solution prepared as follows: The metal was dissolved in concentrated sulphuric acid and warmed to the appearance of white fumes; after cooling, a few cubic centimeters of water boiled and cooled in an atmosphere of carbon dioxide were added, and then 100–150 cc. of a 10 per cent. solution of potassium or sodium pyrophosphate boiled and cooled in carbon dioxide. This solution was slowly heated in a Classen dish to a temperature of 60–62° and electrolyzed at this temperature with a current of 0.025 ampere per sq. dm. and a tension of 1.8 to 2 volts. The end of the reaction was told by the lack of the brown ring in 1 or 2 cc. of the liquid after adding hydrochloric acid and stannous chloride. The precipitate was washed before the current was interrupted.

Baubigny and Chavanne (*C. R.*, **138**, 85; *Bull. Soc. Chim.* (3), **31**, 346) proposed a method for the determination of chlorine and bromine in organic substances, in which they burned the material with a chromic acid mixture in a special apparatus. The chlorine and bromine were absorbed in alkaline sodium sulphite solution. Iodine, if present, would be oxidized to iodic acid in the chromic acid. The chromic acid mixture consists of 30–40 cc. of sulphuric acid, 1 to 1.5 grams of silver sulphate and 8 to 10 grams of potassium bichromate. Lemaitre (*Mon. scient.* (4), **18**, I, 253) determined the amount of sodium perchlorate in commercial nitrates by fusing the nitrate with sodium sulphite and determining the chloride formed by titration with silver salt, using chromate as indicator, or gravimetrically, the sulphate being first removed by treatment with barium nitrate. $NaClO_4 + 4Na_2SO_3 = 4Na_2SO_4 + NaCl$. Jones (*Chem. News*, **89**, 229) found that primary ammonium carbonate solution gives a sharp separation of silver chloride from silver bromide. A simple test for, and method of determination of hypochlorous acid was given by Klimenko (*Z. anal. Chem.*, **42**, 718). This acid and potassium iodide give free iodine, and when hydrochloric acid is then added more iodine, equal in amount to the first, is set free. Chlorine water with potassium iodide yields iodine, but no more if hydrochloric acid be added. If the 4 or 8 per cent. solution of potassium iodide be run into the solution containing hypochlorous acid, the amounts of iodine liberated before and after the hydrochloric acid addition are practically identical. Pontius (*Chem.-Ztg.*, **28**, 59) determined the active chlorine in bleaching-powder, etc., by using the principle that hypochlorous acid in the presence of primary sodium carbonate oxidizes iodide to iodate. He added the chloride of lime solution to some primary sodium carbonate in a dish, then some starch paste and titrated with potassium iodide solution till the next drop caused no blue color. Thilo (*Chem.-Ztg.*, **28**, 866) founded a method for the determination of iodine in the presence of bromine and chlorine upon the observation that on gradual addition of silver salt solution to a solution containing all three halides, iodine is first precipitated completely, and further that iodine will convert silver bromide and chloride into iodide. The end-point of the iodine precipitation, carried out with silver solution of known strength, is shown when a drop of the solution no longer gives a dark spot of palladious iodide on filter-paper freshly dipped in palladious chloride solution. Hennecke (*Pharm. Ztg.*, **49**, 957) titrated iodine in chloroform solution directly with tenth-normal sodium thiosulphate in order to avoid the decomposition of iodine monochloride, which it may contain, thus: $ICl + KI = I_2 + KCl$. Froidevaux (*J. Pharm. Chim.* (6), **20**, 11) offered a method for the detection of fluorine in meat and sausages. He ignited the meat with soda and dissolved the residue in a little boiling water. The filtrate he treated with 2 to 3 cc. of hydrochloric acid and a few drops of helianthine, then saturated ammonium acetate solution till a yellow color was obtained. The addition now of 1 to 2 cc. of 20 per cent. calcium chloride solution would cause a turbidity, if fluorides were present.

Jalowetz (*Allgem. Z. f. Bierbrauerei und Malzfabrikat.*, May, 1904) and Barelt and Schonewald (*Wochschr. f. Brauerei*, **21**, 523, 793) gave figures to show the effect of different kinds of glass upon the results in the Kjeldahl determinations, and the effect is considerable. Brame (*Osterr. Z. f. Berg.-Hutt.*, **52**, 491) gave a rapid method for the determination of nitrogen in iron and steel, in which he obtained the nitrogen as ammonia, passed it into Nessler's reagent and compared it with standard color. Büeler de Florin (*Chem.-Ztg.*, **28**, 1264) recommended for a color scale in working with Nessler's reagent yellow glass plates instead of solutions of known ammonia content. Effront (*Mon. scient.* (4), **18**, 669) based a method for the determination of ammonia and proteid nitrogen in water on the reduction of alkali hypochlorite by ammonia and by albuminous substances, according to this equation: $2NH_3 + 3CaOCl_2 = 3CaCl_2 + 3H_2O + N_2$. He titrated the chloride of lime solution before and after treatment with the water. Another article containing the same principle was published by the same author (*Ber.*, **37**, 4290). Jean (*Ann. Chim. anal. appl.*, **9**, 257) proposed a rapid titration for ammonium sulphate and ammonium chloride. He dissolved the salt in water, added a known amount of a sodium hydroxide solution, made up to a definite volume and titrated one portion directly with half-normal oxalic acid, using lacmoid for indicator. Another portion was diluted and boiled for half an hour, then titrated with the acid. From the difference between these two acid values the nitrogen or the ammonium salts can be calculated. Riegler (*Z. anal. Chem.*, **42**, 677) used the compound $NH_4H_2(IO_3)_3$, which is insoluble in dilute alcohol, as the basis of a gravimetric determination of ammonia. The salt was precipitated by a large excess of iodic acid and was dried over sulphuric acid to constant weight. Or the determination could be made volumetric by treating the precipitated salt with 2 per cent. hydrazine sulphate solution in a nitrometer of some sort and measuring the evolved nitrogen. Sellier (*Bull. de l'Assoc. d. Chim. de Sucr. et Dist.*, **21**, 1063, 1115, 1223) reviewed critically the methods for the determination of ammonia in vegetable products, especially in beets and in the products of the sugar factory and the distillery, deciding that the method of Boussingault of distilling in a vacuum below 40° from magnesium oxide is the most satisfactory. Stähler (*Ber.*, **37**, 4732) found that hydroxylamine could be determined volumetrically by reducing it to ammonia with titanium trichloride or trisulphate, and titrating the excess of trivalent titanium with permanganate, ferric chloride or potassium chlorate. A method for the simultaneous detection of nitrous and nitric acids and for their approximate quantitative determination was offered by Raikow (*Osterr. Chem. Ztg.*, **7**, 557). It depends upon the behavior of the two acids toward diphenylamine in concentrated sulphuric and especially in syrupy phosphoric acid solution. He dissolved 0.2 gram of diphenylamine in 100 cc. of pure concentrated sulphuric acid or of syrupy phosphoric acid, placed 0.5 cc. of this solution in a little flat-bottomed porcelain dish at the edge and added a drop ($^1/_{30}$ cc.) of the liquid to be tested so that the two liquids would run together. Nitrites give a blue color in either solution, nitrates a blue color much more slowly in sulphuric acid solution, and in phosphoric acid solution, characteristic black points with sharply defined edges which are visible even in the solution colored blue by nitrites. The limits of sensitiveness of the reaction are for the sulphuric acid solution 0.0000003 gram potassium nitrate and 0.0000005 gram sodium nitrite and for the phosphoric acid solution 0.0025 gram of nitrate and 0.0000006 gram nitrite. By diluting the solution to be investigated with known amounts of water till under the above conditions the limits of sensitiveness are reached one can calculate the nitrate or nitrite content. Debourdeaux (*C. R.*, **136,** 1668; *Bull. Soc. Chim.* (3), **31,** 3) gave a new volumetric method for the determination of nitric acid. He heated about 0.5 gram of the nitrate in a flask provided with a return flow condenser with 50 cc. of a solution containing 35-40 grams of crystallized oxalic acid, 50 grams of crystallized manganese sulphate and 120 cc. of 66 per cent. sulphuric acid in one liter. The heating was done on a water-bath and after the gas evolution the undecomposed oxalic acid was titrated with permanganate. He (*Compt. rend.*, **138,** 147) applied the same principle to the determination of chlorates, bromates and iodates. Blunt (*The Analyst,* **28,** 313) found that water containing nitrites would give a yellow tint when treated with potassium ferrocyanide.

Lidholm (*Z. angew. Chem.*, **17,** 1452) burned the phosphorus in calcium carbide to phosphoric acid. He provided a flask with a three-holed stopper carrying a dropping funnel, a tube through which hydrogen could enter and a return-flow condenser connected with the simple metal burner having a hole so fine that the acetylene flame would not smoke. The products of combustion were caught in a cylinder 32 cm. long and 5 cm. wide, ending in a 5 mm. tube which was connected with a gas wash-bottle and then with a suction-pump. The carbide was weighed and placed in the flask, then the stream of hydrogen started. The gas was lighted after the air was driven out, then 30 cc. of alcohol were added dropwise to the carbide in the flask, then water. After the gas evolution had stopped, hydrochloric acid was added and the contents of the flask boiled. When the hydrogen flame burned colorless again it was extinguished and the glass cylinder, tubes and wash-bottle were washed with warm ammonia, then with water. The solution was filtered to separate out silica and the phosphoric acid determined as usual with magnesia mixture. Christomanos

(*Z. anorg. Chem.*, **41**, 305) studied the formation of the phosphides of copper and their oxidation, and evolved therefrom a method for the quantitative determination of phosphorus in solution. He weighed the ether or benzene solution of phosphorus into a weighed glass flask, then shook it for some minutes with an excess of a 10 per cent. solution of copper nitrate. A black precipitate was obtained of one of the phosphides of copper. This was heated for fifteen or twenty minutes on a water-bath to cause the precipitate to settle and to drive off the ether or benzene. Then he added to the warm mixture of precipitate and liquid on the water-bath bromine a little at a time with continual shaking; the reaction was violent with the formation of cuprous bromide, perhaps also copper, and phosphorus tribromide which decomposed into phosphorous acid and some phosphoric. He had finally a dark green solution which contained some cupric bromide, all the phosphorus as the two acids, some nitric acid and excess of bromine. The solution was concentrated on the sand-bath with nitric acid to remove bromine and to oxidize all the phosphorous to phosphoric acid, then concentrated further to remove the nitric acid. The phosphoric acid was determined with magnesia mixture. A method for the determination of arsenic which does not depend upon mirrors or color reactions was devised by Cowley and Catford (*Pharm. J.* (4), **19**, 897), who treated 10 cc. of the liquid to be investigated with 2 cc. of hydrochloric acid in a test-tube, sunk a copper spiral most of its length into the liquid, placed the tube in a gently boiling salt-water bath and left it there for an hour. Then they pushed the rest of the spiral down into the liquid and observed whether it was bright after ten minutes, which afforded evidence that all the arsenic had been precipitated. The spiral was now placed in a dish, the arsenic dissolved in bromine water containing some hydrobromic acid, 1 cc. of caustic potash solution added, the mixture boiled to precipitate the dissolved copper and filtered. In the filtrate they reduced the arsenic acid to arsenious and titrated with iodine solution. Pozzi (*L'Industria chimica*, **6**, 144) offered a rapid indirect method for the determination of arsenic, based upon this reaction for dilute solutions: $2AsH_3 + 12AgNO_3 + H_2O = As_2O_3 + 12HNO_3 + 12Ag$. He regulated the flow of hydrogen from his Marsh apparatus to not more than twenty bubbles per minute, added the solution to be analyzed and caught the arsine in two vessels containing 20 cc. of tenth-normal silver nitrate and 1 cc. of ammonia. After three or four hours he determined in 10 cc. of the filtered solution, after acidification with nitric acid, the amount of undecomposed silver nitrate by means of potassium sulphocyanate, using ferric sulphate for indicator. According to Pozzi, 0.1 mg. of arsenic may be detected in this way. Vizern and Guillot (*Ann. Chim. anal. appl.*, **9**, 248) gave this method of detecting arsenic in the crude glycerol of the soap industry. They oxidized 10 cc. of dilute glycerol with 2 grams of hydrogen peroxide of 10–12 per cent. volume content and 2 cc. of hydrochloric acid and a minute's boiling. They then let the mixture cool, put it completely into a large test-tube and added 1 gram of pure zinc with a little copper sulphate. The test-tube was next covered with mercuric chloride paper. After fifteen minutes the under side of the paper would be colored yellow, if there were 1 part of arsenic in 1,000,000 of material. Bougault (*J. Pharm. Chim.* (6), **18**, 509, 545; *Compt. rend.*, **137**, 794) concluded that the presence of antimony trioxide in kermes is more and more doubtful, and that the substance is practically a mixture of antimony trisulphide and acid sodium pyroantimoniate.

A new melting medium for use in the indirect dry way of determining carbon dioxide was proposed by Lutz and Tschischikow (*J. russ. phys.-chem. Ges.*, **36**, 1274). They used sodium metaphosphate and gave its advantages over borax, potassium bichromate and silica. The error caused by its change in weight is negligible, the time required for the operation is short and it may be used even for natural carbonates. It may also be used for the determination of the nitrogen pentoxide of nitrates. The potassium metaphosphate or a mixture of it with the sodium salt does not give satisfactory results. Baroni (*Giorn. Farm. Chim.*, **53**, 481) proposed an easy method of testing the neutrality of glass of vessels. He used neutral solutions of morphine hydrochloride (1 to 2 per cent.), strychnine nitrate (0.5 per cent.), and mercuric chloride (1 per cent.), fused them in the glass to be tested and heated for half an hour in an autoclave at 112°. If the glass is neutral each solution remains unchanged. But if even small amounts of sodium oxide are given up, the morphine salt solution is colored brown with deposition of crystals of the free alkaloid on the sides of the vessel; free strychnine is deposited from the solution of its salt, and yellow, red or brown oxides, finally becoming a brown precipitate, are formed in the mercury salt solution. Van Rijn (*Pharm. Weekblad*, **41**, 1025) determined the alkalinity of glass by simply cleaning it with hydrochloric acid and water, then filling it with distilled water containing phenolphthalein. There must be no reddening after fourteen days. Lucchese (*Ann. Chim. anal. appl.*, **9**, 450, 452) analyzed ferrosilicon by fusion with two or four parts of soda and the same amount of sodium peroxide in a platinum crucible, taking care that pieces of the ferrosilicon did not rest on the bottom of the crucible, and heating very cautiously. The silica was precipitated as usual from the water solution of the melt by means of hydrochloric acid. He gave also a rapid method for the analysis of the same compound, in which he drove off the silicon by evaporating the material to dryness a couple of times with a very little water, 1 cc. of hydrofluoric acid and 1 cc. of nitric acid. The iron remains as ferric oxide, with small amounts of impurities. He weighed the iron oxide, calculated it to metallic iron, and obtained the silicon by difference, neglecting the impurities. Cantoni (*Ann. Chim. anal. appl.*, **9**, 203) rendered his iron-silicon compound soluble by gentle fusion with sodium peroxide, using a copper crucible and removing the copper which dissolved by precipitation with hydrogen sulphide after he had separated the silica.

Metals.—A new method of procedure for the determination of alkalies especially in plants was proposed by Neubauer (*Z. anal. Chem.*, **43**, 14), who precipitated the phosphoric acid, iron, aluminum and magnesium oxides by means of a saturated solution of calcium hydroxide, then the lime with oxalic acid and finally weighed the alkalies as sulphate. Stolberg (*Z. angew. Chem.*, **17**, 741, 769) separated calcium and magnesium by converting both into sulphates, adding a little water to dissolve magnesium sulphate, then a mixture of methyl and ethyl alcohols to throw out the traces of calcium sulphate dissolved. Coehn and Kettembeil (*Z. anorg. Chem.*, **38**, 198) found that the alkaline earth metals could be separated by electrolysis. They tried saturated solutions of the chlorides with varying voltages and determined the current in each case. The voltages were measured against a calomel electrode at 15–18°. As potential differences in the beginning of amalgam formation of the three metals in saturated chloride solution they found between barium and strontium 0.2 volt, between strontium and calcium 0.25 and between barium and calcium 0.45. The differences were still greater when equal concentrations of the three salts were taken. Reichard (*Chem. Ztg.*, **28**, 16) observed that barium, calcium, sodium and potassium peroxides would cause the yellow color in a solution of titanium dioxide in concentrated sulphuric acid, just as hydrogen peroxide does, but that lead and manganese dioxides, cobaltic and nickelic oxides would not. Authenrieth (*Ber.*, **37**, 3882) observed that strontium chromate crystallizes well and is thrown out of solution under conditions that will cause an amorphous precipitation of the barium salt and no precipitation of the calcium salt. He used the reaction for the microchemical detection of strontium and its chromate. He described two modifications. He stated also that he has never found the strontium reaction described by Behrens.

A separation of aluminum from iron was given by Leclere (*C. R.*, **138**, 146). He added to the fairly dilute solution containing a slight excess of sulphuric acid ammonium hyposulphite to reduce the iron, then a great excess of ammonium formate and of hyposulphite and heated to boiling. Aluminum was precipitated as basic formate and was determined by ignition to the oxide. Iron and chromium were separated by Southerden (*Chem. News*, **89**, 183) by melting the dry precipitate of the two in a test-tube with potassium nitrate and adding primary potassium sulphate in small amounts. Chromium is oxidized to chromate. Glasmann (*Z. anal. Chem.*, **43**, 506) gave an oxidimetric method for determining iron and chromium together. The solution was reduced by means of sulphur dioxide in a flask provided with a Bunsen valve, this gas was driven out by boiling and leading in carbon dioxide and the reduced iron was titrated with permanganate. The solution was reduced now with sulphuric acid and zinc, warmed on a sand-bath till it had a constant blue color, indicating the reduction from chromic to chromous oxide, then excess of permanganate was added and the excess titrated with a ferrous salt. Leuba (*Ann. Chim. anal. appl.*, **9**, 303) in his chromite analyses used nitric acid to dissolve the soda melt, but the iron and aluminum hydroxides obtained from this solution with ammonia always contained some chromium. He found this to be due to a reducing action of nitric acid on chromates, it being possible to decompose as much as 9 per cent. of the bichromate with formation of chromic salt by repeated evaporation with nitric acid. The same thing is true with acetic acid. Moulin (*Bull. Soc. Chim.* (3), **31**, 295, 296) based a colorimetric method for the determination of chromium upon the color reaction mentioned by Cazeneuve, that chromium trioxide or a chromate gives with the acetate of diphenylcarbazide a magnificent purple solution. The chromium of the sample was oxidized to chromate by means of hydrogen peroxide and caustic potash, and the liquid neutralized with acetic acid and diluted to 100 or 200 cc. Into each of a series of 100 cc. cylinders was put 2 cc. of the diphenylcarbazide solution (2 grams carbazide, 10 grams acetic acid and 90 per cent. alcohol added to 200 cc.) and 70 cc. of water. Then increasing amounts of a solution of known chromic acid content were added to some of the cylinders, and to others definite amounts of the solution to be tested. Then the cylinders were all filled to 100 cc. and compared in a Dubosc colorimeter after twenty minutes. Moulin described the color reaction in detail and analyzed the products. To the violet compound he ascribed the formula $C_{41}H_{44}N_{10}O_{16}Cr$. Nicolardot (*C. R.*, **138**, 810) separated chromium from vanadium as chlorchromic acid. He melted the sample with four parts of potassium chlorate and one of sodium carbonate, removed small amounts of iron and manganese in the usual manner, then concentrated, dried and melted the salt mass. This was placed in a flask which was connected with a small wash vessel containing sulphuric acid to stop any vanadium that might be carried over, then with a flask filled with dilute sodium hydroxide solution and with a suction-pump. Next fuming sulphuric acid was allowed to flow into the flask through a dropping funnel, at the same time carefully drawing air or hydrochloric acid gas through the apparatus and warming the flask and wash-vessel with sulphuric acid to 60° till the red fumes ceased. Carcano and Namias (*Boll. Chim. Farm.*, **43**, 54) based a volumetric method for the determination of iron in the ferric condition upon this equation: $Fe_2Cl_6 + 2KI = 2FeCl_2 + 2KCl + I_2$. They prevented reoxidation of the ferrous chloride by collecting the iodine in chloroform. The ferric iron solution was diluted till it contained 1 to 2 per cent. of iron, neutralized with sodium carbonate, then concentrated hydrochloric acid was added till the solution contained 5 to 10 per cent. of it, then 2 grams of potassium iodide. After a little standing they added 5 to 10 grams of chloroform and determined the iodine by means of thiosulphate and starch paste. Hollard (*Ann. Chim. anal. appl.*, **9,** 220; *Bull. Soc. Chim.* (3), **31,** 904) stated that he had already used the Carcano and Namias method for the determination of impurities in copper. Tarugi and Silvatici (*Boll. Chim. Farm.*, **43,** 637) gave a new method for the colorimetric determination of iron. One molecule of ferric chloride requires always three molecules of potassium oxalate to decolorize it, and potassium sulphocyanate may be added to the solution for an indicator without influencing the reaction. They recommended the preparation of a fresh typical comparison solution each time titrations are to be made; 5 cc. of tenth-normal ferric chloride, a few drops of potassium sulphocyanate solution and 15 cc. of tenth-normal potassium oxalate. Urbain and Lacombe (*C. R.*, **137,** 792; **138,** 84, 627) in a series of papers gave the results of using the magnesium bismuth double nitrate to help the fractional separation by crystallization of the magnesium double nitrates of the samarium-gadolinium group of rare earths. Lacombe (*Bull. Soc. Chim.* (3), **31,** 570) showed that the double nitrates of the rare earths and manganese possessed advantages for certain separations, notably that of neodymium from praseodymium.

Baumert and Holdefleiss (*Z. f. Unters. Nahr.-Genussm.*, **8,** 177) proposed a method for the detection and determination of manganese in drinking-water. It is a reversal of Winkler's method for the determination of oxygen in water, the equations being as follows:

$$2Mn(OH)_2 + O + H_2O = 2Mn(OH)_3$$

$$2Mn(OH)_3 + 6HCl + 2KI = 2MnCl_2 + 2KCl + 6H_2O + I_2$$

Debourdeaux (*C. R.*, **138,** 88) gave a method whereby the chlorine value and also the hydrochloric acid value (the amount of acid necessary to neutralize the oxide and to free the chlorine) may be determined in one operation instead of in two as formerly. He made use of the decomposition of oxalic acid by the higher oxides of manganese in the presence of dilute sulphuric acid. The equations for manganese dioxide are:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

$$MnO_2 + C_2H_2O_4.2H_2O + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O$$

Those for the other oxides are similar. One molecule of oxalic acid decomposed corresponds to one molecule of chlorine. He heated to gentle boiling in a flask with return-flow condenser the manganese oxides with 50 cc. of a solution composed of 35–40 grams of crystallized oxalic acid, 120 cc. of 66 per cent. sulphuric acid and water to one liter till the oxides were dissolved. Then he diluted this solution and also 50 cc. of the oxalic-sulphuric acid solution each to 200 cc. and determined the oxalic acid in 150 cc. of each by means of permanganate. The chlorine value of the oxides was calculated from the difference in these two oxalic acid values. For the hydrochloric acid value he titrated in the last 50 cc. of each solution the total free oxalic and sulphuric acids, using ammonia and fluorescein. The difference gave the sum of the decomposed oxalic and the combined sulphuric acid and by calculation the hydrochloric acid value desired. A method for the separation of cobalt and nickel from one another and from other metals was patented by Frasch (*Chem. Centrbl.*, 1904, I, 1585). The solution containing these metals was treated with excess of ammonia, filtered and the solution treated with alkali chloride, when the cobalt and nickel are precipitated. He separated out the precipitate and treated it with water, when the nickel ammonia chloride dissolved, while the cobalt ammonia chloride decomposed into hydroxide.

$$Co(NH_3)_2Cl_2.4NH_3 + 2H_2O = Co(OH)_2 + 2NH_4Cl + 4NH_3.$$

Muller (*Bull. Soc. Chim.* (3), **31**, 1300) found that lead and antimony may be satisfactorily determined as sulphides by precipitation from hot acid solutions with hydrogen sulphide, collecting the precipitate on a weighed filter, washing successively with hydrogen sulphide water, 95 per cent. alcohol, a mixture of equal volumes of 95 per cent. alcohol, ether and carbon bisulphide and finally with absolute ether, then drying in a vacuum over sulphuric acid. Rupp (*Z. anal. Chem.*, **42**, 732) tested the action of hydrogen peroxide upon lead, manganese and bismuth salts and found that the bismuth precipitate was bismuthyl hydroxide, while the precipitates of lead and manganese were not of constant composition. Corradi (*Boll. Chim. Farm.*, **43**, 424) determined mercury volumetrically by titrating a known solution of the mercury compound with known potassium iodide solution till the mercuric iodide dissolved. Rose recommended that the end reaction of the Volhard silver determination be sharpened by filtering near the end of the reaction and finishing the titration in the clear filtrate, but Hoitsema (*Z. angew. Chem.*, **17**, 647) pointed out that this causes an error in the results, for the soluble salts can not be washed entirely out of the silver sulphocyanate. Thiel (*Allgemeine Chem. Ztg.*, 4, No. 49) detected silver in the presence of mercurous compounds by treating the precipitated chlorides with bromine water, when the mercury dissolves.

A new volumetric method for the determination of copper was recommended by Griggi (*Boll. Chim. Farm.*, **43**, 392). He titrated the copper salt with a solution containing 1.39 grams of hydroxylamine hydrochloride and 5.6 grams of caustic potash made up to one liter with cold distilled water.

$$(NH_2OH)_2.2HCl + 4(CuSO_4 + 5H_2O) + 10KOH = 2Cu_2O + N_2O + 2KCl + 4K_2SO_4 + 29H_2O.$$

The sulphates of many other metals have a disturbing influence. Cloud (*J. Soc. Chem. Ind.*, **23**, 523) based a determination of small amounts of bismuth upon the fact that lead iodide precipitated in the presence of bismuth is colored more or less dark orange, according to the amount of the latter present. The lead-free solution was treated with 5 cc. of a solution of lead nitrate containing 6 grams of lead per liter and shaken with 25 cc. of a solution of 8.75 grams of potassium iodide per liter, then allowed to stand for fifteen or twenty minutes. The color of the precipitate was then compared with other precipitates which contained known amounts of bismuth. Reichard (*Chem. Ztg.*, **28**, 1024) observed that a drop of bismuth chloride solution would give a magnificent red color with solid brucine or a concentrated solution of brucine, and that the color would remain on evaporation to dryness.

Desvergnes (*Ann. Chim. anal. appl.*, **9**, 321) proposed to determine tungsten by precipitating it from a boiling solution containing it in the form of tungstate by means of a solution of mercuric nitrate containing suspended mercuric oxide. The mixture was again brought to boiling, allowed to settle and the precipitate of mercuric tungstate with oxide ignited. Frabot (*Ibid.*, **9**, 371) noticed independently of Riegler that tungstic acid or Moreigne's phosphotungstic acid reagent and caustic soda would give with uric acid a magnificent blue color. A volumetric method for the determination of tungsten was founded by Kuklin (*Stahl und Eisen*, **24**, 27) upon the fact that metatungstic acid is reduced to tungsten dioxide by excess of zinc, and that this may be oxidized again by permanganate to tungstic acid.

$$5WO_2 + Mn_2O_7 = 5WO_3 + 2MnO.$$

For tungsten in steel he dissolved 2 grams in a mixture of concentrated sulphuric and phosphoric acids and three times as much water, then he added enough permanganate solution so that the solution was colored permanently red, warmed, then cooled and measured it. Half of this solution was treated with sulphuric acid and zinc and heated till the solution took on a port wine color, then allowed to cool in a current of carbon dioxide. After cooling and filtering off the zinc the solution was titrated with permanganate to a rose color. This gave the amount of permanganate needed to oxidize both iron and tungsten dioxide. In the other portion Kuklin determined by the Reinhardt method or by means of stannous chloride and iodine the amount of permanganate needed for the iron alone. A drop of an alcoholic solution of diphenylcarbazide added to a solution of sodium or ammonium molybdate in 30–40 cc. of water acidified with two or three drops of hydrochloric acid gives a magnificent violet color, according to Lecocq (*Bull. de l'Assoc. Belge des Chim.*, **17**, 412). Giolitti (*Gaz. chim. ital.*, **34**, II, 166) determined uranium by reducing the salt, if uranyl, and then precipitating the tetravalent uranium by means of hydrofluoric acid in a platinum dish, washing by decantation, filtering through a rubber funnel and igniting in an open crucible to uranous-uranic oxide. Glasmann (*Ber.*, **37**, 189; *J. russ. phys.-chem. Ges.*, **36**, 317) used the following reaction for the iodometric determination of uranium:

$$3UO_2(NO_3)_2 + 5KI + KIO_3 + 3H_2O = 3UO_2(OH)_2 + 6KNO_3 + 3I_2.$$

The iodine is distilled into a receiver and titrated with thiosulphate. Dreher (*Centrbl.*, 1904, II, 67) patented a method for the separation of titanic acid from mixtures of it with metals like iron, aluminum, etc. Instead of reducing the solution in mineral acid by means of sulphur dioxide he used such metals (tin, zinc, iron, sodium amalgam) as would give hydrogen with the acid of the solution (which might be sulphuric or alkali bisulphate, hydrochloric, hydrofluoric or an organic acid like oxalic). The acid titanium solution could also be electrolyzed at the cathode where hydrogen is evolved. The titanic acid present would be thrown out as a bluish precipitate, if the solution were weakly acid or on approximate neutralization. This lower form of oxidation is changed again in the air or by an oxidizing agent to the white titanic acid. Dreher stated that this titanic acid is free from the metals and that it is precipitated in the easily soluble form. Campagne (*Bull. Soc. Chim.* (3), **31**, 962) gave a method of detection and a volumetric method of determining vanadium and chromium together. The solid was fused with a mixture of equal parts of sodium nitrate and carbonate, the mass extracted with water, filtered, the filtrate acidified with sulphuric acid and shaken with a few cubic centimeters of hydrogen peroxide and ether. With both metals present the aqueous solution would be red, the ether blue. For the volumetric determination the solution was repeatedly evaporated with hydrochloric acid to form vanadyl dichloride ($VOCl_2$). Free sulphuric acid must be absent. At the end of the reduction the substance was treated with 10 cc. of pure sulphuric acid and heated on a sand-bath till white fumes appeared. Chromic sulphate and hypovanadic sulphate ($V_2O_2(SO_4)_2$) are formed. This was taken up with water and titrated at the ordinary temperature with permanganate to oxidize the vanadium.

$$5V_2O_2(SO_4)_2 + 2KMnO_4 + 8H_2SO_4 = 5V_2O_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

At the end of the titration an excess of 10 per cent. permanganate was added and the solution boiled to oxidize the chromium to chromate, the excess of permanganate removed by pieces of filter-paper and the solution filtered after cooling. The chromium was then reduced by means of a known excess of ferrous ammonium sulphate solution and the excess titrated back with permanganate. In reality instead of titrating the excess of ferrous salt the amount of vanadyl sulphate ($V_2O_2(SO_4)_3$) reduced by it to hypovanadic sulphate ($V_2O_2(SO_4)_2$) was titrated. Glasmann (*J. russ. phys.-chem. Ges.*, **36**, 314) separated vanadium from iron and aluminum by means of potassium iodide and iodate and removal of the precipitated iodine with sodium thiosulphate.

$$V_2O_5 + 4HI = V_2O_3 + 2H_2O + 2I_2.$$

$$Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3I_2.$$

A method for the determination of tin in tin plate was given by Angenot (*Z. angew. Chem.*, **17**, 521). He cut the plate into pieces about 1 cm. square, heated them in a little iron crucible to quiet fusion for ten minutes with twice as much sodium peroxide, allowed the mass to cool and dissolved it in a covered beaker in 100 cc. of cold water, washed into a 250 cc. flask, filled to the mark and filtered. He acidified 200 cc. of the filtrate with dilute sulphuric acid (1 : 2), boiled for five minutes, washed the precipitate, then ignited it to stannic oxide.

Donau (*Monatsh. Chem.*, **25**, 545, 913) gave a microchemical test for gold, and the colors of the borax bead caused by some of the noble metals in colloidal solution. Silk fiber, prepared from crude silk by three or four hours' treatment with 10 per cent. potassium or sodium hydroxide solution, washing and mordanting with stannous chloride and pyrogallol, gives with specially prepared chlorauric acid solutions red colors by means of which Donau said the delicacy of the present microchemical tests could be increased 1000 times. The color is not destroyed by acids or bases but is by chlorine or bromine, which shows the color to be due to gold. The red color is due to colloidal gold; blue or dark colors are due to more or less coarse gold particles. Gold gives a ruby-red color to the borax bead, silver a yellow and platinum a fawn-color. A volumetric determination of platinum resting on the difficult solubility of thallous chlorplatinate was given by Rupp (*Arch. der Pharm.*, **242**, 143). He used a 2 to 2.5 per cent. solution of thallous nitrate standardized against potassium chromate thus: Ten cc. of a 4 per cent. solution of the chromate of known thiosulphate titer were treated in a 100 cc. flask with water and about 1 gram of precipitated calcium carbonate, 10 cc. of thallium solution were added, the volume made up to 100 cc. and the whole mixed and filtered. Of the filtrate 25 cc. were treated with 50 cc. of water, 1 to 2 grams of potassium iodide, about 5 cc. of 25 per cent. hydrochloric acid and titrated after five minutes with twentieth-normal thiosulphate solution. The platinum solution, which may contain only a very little hydrochloric acid, was put in a 50 or 100 cc. flask with a measured excess of the thallium solution, allowed to stand for an hour in the cold, made up to the volume, filtered through a double filter and the excess of thallium determined as above in 25 or 50 cc. of the filtrate.

Hollard and Bertiaux (*Bull. Soc. Chim.* (3), **31**, 102, 900, 1124, 1128, 1131; *C. R.*, **138**, 1605, 139, 366) have published half a dozen articles dealing largely with electrolytic separations of these elements: Copper, arsenic and antimony, nickel and zinc, zinc and iron, bismuth and copper and bismuth and lead; also the analyses of commercial lead and tin, which they accomplished largely by electrolytic methods.

Hydrazine sulphate was proposed many times as a reagent useful in making quantitative determinations of various elements, most of the methods being volumetric. The collection follows. Roberto and Roncali (*L'Industria chimica*, **6**, 93, 178) used it to determine oxidizing substances, such as bleaching-powder, permanganate and bichromate.

$$N_2H_4.H_2SO_4 + Cl_2 = N_2 + 4HCl + H_2SO_4.$$

$$N_2H_4.H_2SO_4 + O_2 = N_2 + 2H_2O + H_2SO_4.$$

For the chlorine in bleaching-powder they put 100 cc. of water, 2 to 3 grams of hydrazine sulphate and 30 cc. of dilute sulphuric acid into a flask which was closed by a cork carrying a delivery tube and a funnel tube. The contents of the flask were brought to boiling, and after air was driven out of the flask, 100 cc. of a solution equivalent to 1 gram of bleaching-powder were added with continued boiling, then finally 30–40 cc. of water. The nitrogen was measured as usual and the chlorine calculated. The other two determinations were similar. Another oxidizing agent, potassium persulphate, was similarly determined by Pannain (*Gaz. chim. ital.*, **34**, I, 500). He used a Lunge nitrometer, and set the hydrazine free by concentrated caustic potash.

$$2K_2S_2O_8 + N_2H_4.H_2SO_4 + 6KOH = 5K_2SO_4 + N_2 + 6H_2O.$$

The Riegler (*Z. anal. Chem.*, **42**, 677) determination of ammonia by precipitation of monoammonium triiodate and subsequent treatment of the precipitate with hydrazine sulphate has already been mentioned. This author (*Ibid.*, **43**, 205) again recommended hydrazine sulphate as a means of determining gasometrically calcium, strontium, barium and potassium, also copper. He first precipitated these elements as iodates and then treated the iodates with hydrazine sulphate.

$$Ca(IO_3)_2 + 3N_2H_4.H_2SO_4 = CaSO_4 + 2HI + 6H_2O + 3N_2.$$

Rimini (*Atti R. Accad. dei Lincei Roma* (5), **12**, II, 376; *Gaz. chim. ital.*, **34**, I, 224) determined hydrazine itself by the nitrogen evolved when the hydrazine salt was treated with mercuric chloride and caustic potash. A molecule of hydrazine salt yields a molecule of nitrogen. The method might be used for mercury. De Girard and de Saporta (*Bull. Soc. Chim.* (3), **31,** 905) gave again the copper determination of Purgotti, using hydrazine sulphate in alkaline solution, and corrected his equation. They suggested the use of the method for the determination of glucose, the cuprous oxide obtained in the usual manner being dissolved up and oxidized, then determined volumetrically. They gave also a direct determination of sodium nitrite.

$$2NaNO_2 + N_2H_4.H_2SO_4 = N_2 + Na_2SO_4 + 2NOH + 2H_2O.$$

Gutbier (*Sitzungsber. d. phys. med. Soc.*, 1904, p. 130) recommended hydrazine sulphate as a means of reducing tellurium for the quantitative determination, and with Metzner and Lohmann (*Z. anorg. Chem.*, **41,** 291) used a hydrazine salt for the reduction of selenium. Jannasch with Bettges, with Rostosky and with Stephan (*Ber.*, **37,** 1980, 2210, 2219 and 2441) used hydrazine salts for the separation of mercury from molybdenum and tungsten, of palladium from nearly all other metals and of platinum likewise from other metals.

NOTE.

On the Detection of Nickel.—The potassium nitrite test for cobalt in presence of other metals, especially nickel, orginally proposed by Fischer,[1] is not very generally used in qualitative analysis, owing probably to the fact that at least twenty-four hours is required to effect complete removal of the cobalt.

Since cobalt is usually more readily detected than is nickel, it may be of interest to give the following modification of Fischer's method by which immediate and complete removal of cobalt can be effected. Since, however, pure nickel solutions give precipitates with this method, which, though slight, could readily be mistaken for cobalt, this test is not applicable for detection of the latter element, and is proposed only as a means for the rapid removal of cobalt, preliminary to testing for nickel.

The method depends on the well-known fact that potassium cobaltinitrite is much less soluble in strong solutions of potassium salts than in water. The procedure is as follows: A portion of the solution is tested for cobalt. In case cobalt is found the remainder, which must be neutral or alkaline, is saturated with potassium chloride, leaving an excess of the solid salt present, and treated with either a little solid potassium nitrite or with

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[1] Pogg. *Ann.*, **74,** 124 (1849).