

## Analytical Chemistry.

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**Apparatus for Electro-analytical Determinations with a Mercury Cathode.** PAUL BAUMANN (*Chem. Zeit.*, 1911, 35, 854—855).—Details are given of an improved form of the mercury cathode vessel described by Böttger (Abstr., 1909, ii, 619), the object of the improvement being to facilitate the running-off of the electrolyte from the mercury at the end of the electrolysis, and also to trap any mercury or amalgam which may be carried over. This object is attained by inserting a stoppered tube, opening just above the level of the mercury, into the side and near the bottom of the vessel, there being a bulb in the tube between the stopcock and the vessel; the bulb acts as a trap for any mercury carried over.

The anode, which may be stationary or rotated, is a two-decker gauze electrode, similar in shape to the Hildebrand electrode (Abstr., 1907, ii, 574), and strengthened by appropriate struts.

The apparatus may be used for separations by graded potential. It cannot be heated directly, for fear of breaking, so that when the heat generated by the current used for electrolysis is insufficient, a special heater must be used. This consists of a platinum wire heated electrically and enclosed in a glass tube filled with paraffin oil; the glass tube is then immersed in the electrolyte when heating is necessary.

T. S. P.

**Detection of Gas in Sealed-tube Reactions.** WILLIAM H. WARREN (*J. Amer. Chem. Soc.*, 1911, 33, 1417—1418).—The author seals on to the Carius tube a tap of the same glass, and is thus enabled to collect any gas formed during the reaction.

E. J. R.

**Estimation of Organic Matter in Waters by means of Permanganate.** HERMANN NOLL (*Zeitsch. angew. Chem.*, 1911, 24, 1509—1518).—The author's experiments show that in the estimation of organic matter in water by Kubel's method with permanganate, the direct action of sulphuric acid on permanganate and on any manganese dioxide formed is of no account so far as loss of oxygen is concerned. The sulphuric acid present hinders the formation of manganese dioxide from manganese sulphate and permanganate.

The interaction between manganese sulphate and permanganate takes place according to the equation given by Roscoe and Schorlemmer, namely,  $3\text{MnSO}_4 + 2\text{KMnO}_4 + 2\text{H}_2\text{O} = 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$ . Manganese dioxide acts auto-catalytically on this reaction, but in water analysis, by Kubel's method, the catalytic effect is negligible.

In the determination of organic matter, the permanganate must always be in considerable excess, otherwise any manganese dioxide which may be formed will take part in the oxidation and the results will be too low. The addition of manganese sulphate to waters containing much chloride is therefore not to be recommended, since the

formation of manganese dioxide is thereby increased. It is better in such cases to use Schulze's method.

The author considers that Kubel's method is satisfactory.

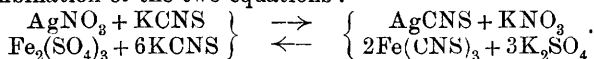
T. S. P.

**A New Reaction for the Detection of Hydrogen Peroxide.** O. VON SOBBE (*Chem. Zeit.*, 1911, 35, 898).—An ammoniacal silver nitrate solution is recommended for the detection of small quantities of hydrogen peroxide. A characteristic grey opalescence or precipitate is obtained. The test is even more delicate than the reaction with potassium iodide and starch usually employed.

L. DE K.

**Volhard's Method for the Estimation of Chlorine in Potable Waters.** A. T. STUART (*J. Amer. Chem. Soc.*, 1911, 33, 1344—1349).—In the determination of chlorine in drinking waters by Volhard's method, the author met with various discrepancies, which led to the following investigation. Two c.c. of silver nitrate solution (1 c.c. = 0.001 gram Cl) were added to 100 c.c. of water, and the solution titrated with potassium thiocyanate of strength equivalent to the original silver nitrate solution. Varying volumes (from 0.1 to 100 c.c.) of a 1% solution of ferric sulphate solution were added as indicator. It was found that various quantities of thiocyanate solution were required, the figures showing that in titrating 2 c.c. of silver nitrate, using 1 c.c. of indicators varying in strength from 1 to 10%, the readings may vary between 1.80 and 2.09 c.c. This represents an error not permissible for work of extreme accuracy, involving in its limits 2.9 parts per million of chlorine.

The error is caused by equilibria set up, which may be represented by a combination of the two equations :



The end point is also influenced by the dissociation of the ferric thiocyanate.

The conclusion is drawn that the method is only applicable in water analysis when very small amounts of silver nitrate, not greater than 0.2 c.c., in excess of that required are added.

Similar, but less, variations occur with *N*/10-solutions when large volumes of indicator solution are added.

T. S. P.

**Estimation of Iodine in Thyroid.** ATHERTON SEIDELL (*J. Biol. Chem.*, 1911, 10, 95—108).—A large number of estimations of iodine in the thyroids of different animals are given; a good deal of irregularity is noted, but the theory that this is due to seasonal influences is regarded as inconclusive. Although the Hunter method of analysis is admitted to be the best, the conclusions drawn from results obtained by the Baumann process are not invalidated.

W. D. H.

**Estimation of Small Quantities of Iodine in Animal Fluids.** R. BERNIER and G. PÉRON (*J. Pharm. Chim.*, 1911, [vii], 4, 151—157).—The application of the method already described for the

estimation of iodides (this vol., ii, 435) to organic liquids is rendered difficult in many cases by the presence of nitrites, formed by the action of permanganate on carbamide and other similar substances originally present in such products. The nitrites may be eliminated by the use of carbamide or ammonium salts in presence of acids. The following modification of the original process is given: Ten to twenty c.c. of urine, to which 0.5 gram of potassium hydroxide has been added, is evaporated to dryness in a nickel basin at 100°, and the residue calcined over a spirit lamp. The cold calcined residue is dissolved as far as possible in a little distilled water, the exhaustion of the soluble matter being completed with a 10% solution of sodium chloride. To the filtered extract potassium permanganate is added in excess, and the excess destroyed by alcohol. The cold solution is then made up to 110 c.c. and 100 c.c. of filtrate collected. To this 1 gram of ammonium chloride and 10 c.c. of acetic acid are added, and the whole boiled during five to ten minutes. The rest of the process is carried out as described previously (*loc. cit.*). The experimental difficulties met with in certain cases are described, with methods of overcoming them. The process is applicable to normal and pathological urines, blood, blood serum, and various liquids of the organism whether physiological or pathological in origin. A number of typical results with such fluids are quoted.

T. A. H.

**Estimation of Halogens in Organic Compounds.** THEODOR ST. WARUNIS (*Chem. Zeit.*, 1911, 35, 906—907).—The process may be applied in the case of solid substances or even liquids if they are not readily volatile. 0.2—0.3 Gram of the powdered substance is mixed in a spacious nickel crucible by means of a platinum wire with an intimate mixture of 10 grams of powdered potassium hydroxide and 5 grams of sodium peroxide. After putting on the lid, the crucible is heated in an air-bath at 75°, or at most 85°. When the mass begins to agglomerate, a gradually increased heat is applied by means of a very small flame until the mass has turned liquid, and it is kept in that condition for some time.

The fusion is dissolved in water, and gradually acidified with dilute nitric acid; if any iodine should be liberated, the solution should be decolorised by cautiously adding sulphurous acid. The halogen is then determined by means of silver nitrate, gravimetrically or volumetrically as usual.

L. DE K.

**Estimation of Halogens in Lipoids.** H. CAPPENBERG (*Pharm. Zeit.*, 1911, 56, 677).—One gram of the substance is placed in a porcelain crucible, a piece of cotton-wool is placed over it, and 10 c.c. of a 10% solution of potassium hydroxide in methyl alcohol are added. The contents of the crucible are evaporated to dryness at a temperature below the boiling point of the alcohol, then ignited over a low Bunsen flame for one hour, and the carbonised residue is dissolved in 100 c.c. of hot water. The solution is filtered, rendered acid with nitric acid, and the halogen is precipitated by the addition of silver nitrate.

W. P. S.

**Estimation of Dissolved Oxygen Absorbed by Sewage Effluents containing Nitrites and of Nitrites in Sewage Effluents and Water.** ROBERT W. CLARKE (*Analyst*, 1911, 36, 393—396).—*Estimation of Dissolved Oxygen Absorbed.*—The effluent is diluted, say, ten times with pure tap water, and five bottles of known capacity (300 c.c.) are completely filled therewith. The amount of oxygen present at the start and after one, two, and five days respectively is then determined by Winkler's manganese method (introduction of manganous chloride and sodium hydroxide containing potassium iodide; after acidifying with hydrochloric acid, the iodine liberated, which represents free oxygen, is estimated as usual). The author, however, recommends neutralising the free acid before titration with magnesium carbonate; nitrites will then not interfere. The difference in amount of free oxygen at the commencement and after a given interval gives the amount of oxygen absorbed.

*Estimation of Nitrites.*—A tall bottle holding 500 c.c. is filled with the nitrite-containing water or effluent to within 20 c.c. of the whole content. To this are added 4 c.c. of 33% manganese chloride, and 12 c.c. of the usual sodium hydroxide and potassium iodide solution with an extra gram of the latter are added. After shaking the stoppered bottle and allowing it to stand overnight, all free oxygen will have disappeared from the liquid, which, however, retains the nitrite. The clear liquid is now siphoned off into a 300 c.c. bottle, 3 c.c. of hydrochloric acid are added, and, after neutralising the excess of this with magnesium carbonate, the iodine liberated, representing the nitrite, is titrated with very dilute standard thiosulphate.

L. DE K.

**New Method of Estimating the Various Elements of an Organic Substance.** (1) Substance Containing C,H,O,N. (2) Substance Containing C,H,O,N,S. (3) Substance Containing C,H,O,N,S,Cl,Br,I. J. A. A. AUZIES (*Bull. Soc. chim.*, 1911, [iv], 9, 814, 815, 815—819).—For a substance containing carbon, hydrogen, oxygen, and nitrogen, the combustion tube, otherwise arranged in the ordinary manner, is filled with specially prepared thoria in place of cupric oxide. The water and carbon dioxide are collected in the usual way, and the nitrogen peroxide formed in the combustion is collected in a solution of cuprous chloride in hydrochloric acid, placed between the usual calcium chloride tube and the potash bulbs. The nitric peroxide formed is estimated by titrating the absorbent solution with standard stannous chloride.

When the substance to be burnt contains sulphur, a portion of the tube is filled with lead peroxide, or, better, the thoria and the lead peroxide are each enclosed in boats of special form. The sulphur is oxidised to sulphur dioxide by the thoria, and this is absorbed by the peroxide to form lead sulphate, which is determined gravimetrically.

When halogens are present, a third boat containing silver chromate is introduced. After the combustion is complete, the partly transformed chromate is treated with ammonia solution, which dissolves the chromate and chloride, the latter being recovered quantitatively by adding acetic acid to the solution and treating the precipitate with

potassium cyanide solution. The residue, insoluble in ammonia solution, is treated with potassium cyanide solution, which dissolves the silver iodide, but leaves the bromide unaffected. Results of simultaneous determinations of the eight elements by this process are quoted. The special boat recommended is figured in the original.

T. A. H.

**The Hyperbolæ of Furnace Gas Constituents.** ERNST LÁSZLÓ (*Chem. Zeit.*, 1911, 35, 994—996).—The author develops equations by means of which, having determined the percentage of carbon dioxide in furnace gases, the percentage of oxygen and nitrogen in the same can also be calculated, and also the ratio of the air passed into the furnace to that which is theoretically necessary for complete combustion. It is assumed that the ratio of nitrogen to oxygen in the air is known, and also the value of  $l$ , when the hydrocarbon burned has the formula  $C_mH_{lm}$ .

T. S. P.

**Estimation of Silicon in Iron containing much Graphite.** C. REICHARD (*Pharm. Zentr.-h.*, 1911, 52, 939—940).—One gram of the finely-divided iron is heated in a platinum crucible for fifteen minutes over a blast-flame, or for one hour over a Bunsen flame, and then dissolved in 25% hydrochloric acid. The solution is decanted from the small quantity of insoluble matter, and the latter is treated with fuming nitric acid. After the two acid solutions have been mixed together, the insoluble graphite is collected on a filter, washed, and ignited in an atmosphere of oxygen. The portion of the silica which remains in the acid filtrate is estimated in the usual way.

W. P. S.

**The Oxidation of Hydrazine. V. Reaction between Potassium Iodate and Hydrazine Sulphate.** C. F. HALE and H. W. REDFIELD (*J. Amer. Chem. Soc.*, 1911, 33, 1353—1362. Compare Brown and Shetterly, *Abstr.*, 1910, ii, 233, 568).—The authors show that the oxidation of hydrazine sulphate by potassium iodate proceeds quantitatively in accordance with the equation given by Rimini (*Abstr.*, 1906, ii, 897), namely,  $5N_2H_4 \cdot H_2SO_4 + 4KIO_3 = 5N_2 + 12H_2O + 2K_2SO_4 + 3H_2SO_4 + 2I_2$ . In each experiment carried out the excess of iodate was determined, and also the volume of nitrogen evolved. The reaction is the same, whether the hydrazine is added to the potassium iodate in the cold (in an atmosphere of carbon dioxide) or at the boiling temperature (in an atmosphere of steam).

The method of procedure recommended is as follows: About 0.3 gram of the hydrazine salt is dissolved in 50 c.c. of water in a 300 c.c. narrow-mouthed conical flask. A measured volume of potassium iodate solution (7.1045 grams per litre) is then added, so that there are 5—10 c.c. in excess. The solution is diluted to 200 c.c., and boiled for thirty minutes over a free flame to expel the iodine. After cooling, potassium iodide and dilute (1:4) sulphuric acid are added, and the liberated iodine is titrated with  $N/10$ -thiosulphate.

The chief disadvantage of the method lies in the length of time required for the expulsion of the liberated iodine. T. S. P.

**Estimation of Nitric Nitrogen in Gun Cotton, Nitroglycerol, and Similar Products.** HENRI PELLET (*Ann. Chim. anal.*, 1911, 16, 294—296).—Schloesing's apparatus is preferred. In the case of gun-cotton or saltpetre (used for a check experiment) the substance is placed in the flask containing distilled water, which is then boiled until all the air has been expelled. A solution of ferrous ammonium sulphate strongly acidified with hydrochloric acid is introduced from the funnel tube, and the nitric oxide expelled on boiling is collected and measured.

In the case of substances which suffer volatilisation on boiling, such as nitroglycerol or nitric ethers, the iron solution is placed in the flask, and, after expelling the air by boiling, the nitrate is gradually added in dilute solution from the funnel tube. L. DE K.

**Estimation of Nitrites in Waters.** GUSTAVE BLANC (*J. Pharm. Chim.*, 1911, [vii], 4, 205—212).—It is shown that Trommsdorff's method is bad in principle, since the nitric oxide formed by the interaction of zinc iodide with nitrous acid is oxidised in contact with the air, forming more nitrous acid, which reacts with more of the iodide, so that the amount of iodine liberated and titrated may be far in excess of that corresponding with the amount of nitrite originally present. Test analyses confirmed this. Griess' method, on the contrary, was found experimentally not to be subject to any error of this kind.

T. A. H.

**Some Sources of Error in the Gasometric Estimation of Nitrates and Nitrites by Schloesing's or Piccini's Methods.** OTTO RUFF and EWALD GERSTEN (*Zeitsch. anorg. Chem.*, 1911, 71, 419—426).—The presence of arsenites or sulphides in a solution of nitrates or nitrites gives rise to errors in the gasometric estimation. In the estimation of nitrates, in which an acid solution of ferrous chloride is required, the presence of arsenites causes a loss of nitric oxide, owing to the formation of nitrous acid, which passes over into the nitrometer. Arsenites only reduce nitrates in acid solution. Nitrites may be estimated satisfactorily, even in presence of arsenites, if the solution is kept neutral. Sulphides, however, prevent the estimation of nitrates or nitrites, the nitrous acid being partly reduced to ammonia. C. H. D.

**The Quantity of Nitric Acid Present in Wines.** J. TILLMANS (*Zeitsch. Nahr. Genussm.*, 1911, 22, 201—207).—The author finds that nitric acid is a natural constituent of practically all German wines, the quantity present varying from a mere trace to 18.75 mg. ( $N_2O_5$ ) per litre. The detection of nitric acid in wine does not, therefore, indicate the presence of added water in the wine. The diphenylamine-sulphuric acid method was employed for the estimation of the nitric acid; this method has been described previously (this vol., ii, 767),

but in the case of wine it is necessary to evaporate the diluted sample after the addition of animal charcoal in order to remove substances which interfere with the reaction, the estimation being then made on the evaporated solution diluted with water to its original volume.

W. P. S.

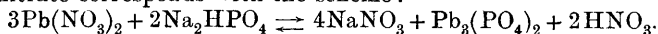
**Estimation of Phosphorus in Wine.** JEAN DORMANE (*Bull. Assoc. chim. Sucr. Dist.*, 1911, 29, 63—67).—The total phosphorus in wine is estimated by treating the dry residue from 200 c.c. with calcium hydroxide and heating on a sand-bath. It is then powdered, placed in a platinum boat, and heated in a porcelain tube in a current of air. The portion of the porcelain tube behind the platinum boat is filled with potassium carbonate. The whole tube is heated for two to three hours. The ash and the alkali are dissolved in dilute hydrochloric acid, and the phosphates estimated by means of ammonium-magnesium solution.

In estimating the phosphorus as phosphates, the residue from 100 c.c. of wine is extracted with cold dilute hydrochloric acid, and the phosphates in the filtrate precipitated in the usual manner.

The same process is employed for estimating the organic phosphates, except that the residue is boiled for an hour and a-half with stronger hydrochloric acid. The amount of phosphorus present as inorganic phosphates is deducted from the results.

N. H. J. M.

**Titration of Phosphoric Acid.** M. WAGENAAR (*Pharm. Weekblad*, 1911, 48, 845—850).—For determining the three hydrogen ions of phosphoric acid, the author recommends the following procedure: For the first ion the solution is tinted red with methyl-orange, and titrated with alkali until yellow; for the second, the titration is repeated after addition of phenolphthalein to the yellow reaction-mixture; for the third, excess of lead nitrate is added, and the rose-red solution titrated with sodium hydroxide. The action of the lead nitrate corresponds with the scheme:



A. J. W.

**The Alkalimetry of Magnesium Ammonium Phosphate and Acidimetry of Ammonium Phosphomolybdate.** FRANZ HUNDESHAGEN (*Zeitsch. öffentl. Chem.*, 1911, 17, 283—294, 302—309, 322—324).—The author again recommends his titration process (*Abstr.*, 1895, ii, 84), which, however, had been previously worked out by Stolbe, and consists in washing the ammonium magnesium phosphate obtained in the usual way with alcohol until free from ammonia; the precipitate is then dissolved in a slight excess of standard acid, and the solution titrated with standard sodium carbonate, using methyl-orange as indicator. Twenty-five test analyses are given, showing the accuracy of the method. If arsenic acid is suspected, a previous separation of this substance should be effected by means of hydrogen sulphide, or else its amount present in the precipitate must be determined and allowed for. One c.c. of *N*/10-acid = 0.003552 gram of phosphoric anhydride, or 0.002016 gram of magnesium oxide. When



the process is applied in the so-called "citrate method," the triple phosphate should be purified by re-dissolving it in hydrochloric acid, and reprecipitating it with ammonia, after adding a little of the usual citrate solution and a little magnesium mixture; it will then be free from calcium and fit for titration.

Good results are also obtained by the author's well-known molybdate method, in which the yellow precipitate is dissolved in standard alkali, the excess of which is then titrated with standard acid, using phenolphthalein or litmus as indicator. One c.c. of *N*-alkali = 0.003078 gram of phosphoric anhydride. Operators are again reminded of the precautions to be taken to ensure the formation of a pure yellow precipitate. A microscopical test will prove the presence or absence of free molybdic acid.

L. DE K.

**Estimation of Arsenic in Toxicological Analysis.** W. NEY (*Pharm. Zeit.*, 1911, 615—616).—A weighed quantity of the substance, such as a portion of an animal organ, is distilled with 100 c.c. of hydrochloric acid, D 1.19, 2 grams of potassium bromide, and 5 grams of hydrazine sulphate until the mixture has been reduced to a syrupy consistence. The distillate is received in 200 c.c. of water, and the arsenic trichloride is then titrated with iodine solution in the presence of sodium hydrogen carbonate.

W. P. S.

**Treatment of Insoluble Residues.** ERICH EBELER (*Zeitsch. anal. Chem.*, 1911, 50, 610—614).—Lead chloride, together with any lead sulphate, is best removed by heating the insoluble matter with ammonium nitrate (40 c.c. of ammonia, D 0.925, and 67 c.c. of nitric acid, D 1.3325). Complex cyanides and insoluble (ignited) oxides may, generally, be rendered soluble by fusion at not too high a temperature with potassium hydrogen sulphate; the mass is then extracted with water containing a few drops of hydrochloric acid. The filtrate is tested as usual for metals, and the undissolved matter is examined for silver by treating with dilute sulphuric acid and a little zinc. When reduction is complete, the precipitate is washed with hot water and the excess of zinc and the silver are dissolved in dilute nitric acid; the silver is then tested for as usual.

The residue, which may contain antimonious oxide, stannous oxide, stannous phosphate, and perhaps silica, is collected, ignited, and weighed. It is then fused in a covered crucible at a gentle heat with two or three times its weight of the usual sulphur-potassium carbonate mixture. The mass is extracted with hot water, and the solution is treated according to one of the usual methods for the separation of tin, antimony, etc.

It is advisable to examine the undissolved portion of the fusion for alkaline earths and silica. This is done by fusing with anhydrous sodium carbonate over the blow-pipe. The mass is extracted with water, and both solution and residue are then examined by the usual methods for silica and alkaline earths respectively.

L. DE K.

**Separation Scheme without the Use of Hydrogen Sulphide.** ERICH EBELER (*Zeitsch. anal. Chem.*, 1911, 50, 603—609).—A slight modification of the process described some time ago (Abstr.,



1906, ii, 126). It is recommended first to remove the arsenic by distilling the mixture with fuming hydrochloric acid with addition of hydrazine bromide; the arsenic is then tested for in the distillate. In the presence of complex cyanides these are destroyed by boiling for half an hour in a reflux condenser with a mixture of equal volumes of fuming nitric and hydrochloric acids. Before applying the course without the use of hydrogen sulphide, the hydrochloric acid is expelled by repeated evaporation with nitric acid.

Uranium remains with the alkaline earths as a complex hydroxyl-amine compound of uranic acid, but is readily separated by a process communicated previously (Abstr., 1908, ii, 987); the alkaline earths are separated by the author's hydrochloric acid process (Abstr., 1909, ii, 347), but instead of a hardened filter an asbestos filter is now recommended.

The alkalis should be tested for in a separate portion of the mixture. The method used for silicates (heating with ammonium chloride and calcium carbonate) will be found very suitable. L. DE K.

**Method for the Reduction of Potassium Platinichloride in the Estimation of Potassium by the Platinum Process.** A. FIECHTER (*Zeitsch. anal. Chem.*, 1911, 50, 629—632).—The author recommends the process based on the reduction of the potassium platinichloride by means of magnesium ribbon and dilute hydrochloric acid at the boiling point, using only a few drops of acid at first. If 1 gram of the substance guaranteed to contain 5% of  $K_2O$  is taken for analysis, 0.2 gram of magnesium ribbon is required; for 20%, 0.5, and for 50%  $K_2O$ , 0.8—1 gram of magnesium will be sufficient.

L. DE K.

**Estimation of Calcium Nitrate and Calcium Nitrite.** ALBERT STUTZER and GOY (*Chem. Zeit.*, 1911, 35, 891).—In the estimation of calcium nitrite and nitrate in the technical products made by the combustion of atmospheric nitrogen, Busch's method (Abstr., 1906, ii, 392) gives unsatisfactory results, and the authors prefer to estimate the nitrite by titration with permanganate and then to estimate the total nitrogen in the oxidised liquid with "nitron."

Since "nitron" is very expensive, the authors recommend that the total nitrogen be determined by reduction to ammonia with Devarda metal (50% Cu, 45% Al, 5% Sn) and distillation of the ammonia into excess of standard sulphuric acid. T. S. P.

**Analysis of "Nitrolime."** HUBERT KAPPEN (*Chem. Zeit.*, 1911, 35, 950—952).—A series of experiments from which it appears that the total nitrogen in "nitrolime" is best estimated by treating 0.5 gram of the sample with 10 c.c of water before boiling with 30 c.c. of sulphuric acid (Kjeldahl process). Addition of sodium thiosulphate, salicylic acid, and zinc dust does not seem to produce the effect expected by Monnier. Full particulars are found in the tables of the original paper.

For the estimation of cyanamide nitrogen, Perotti's silver process is recommended. In recently prepared samples the results agree very

well with the total nitrogen according to Kjeldahl. Old and badly stored samples often contain dicyanodiamide. In the absence of dicyanodiamidine it is best estimated by Caro's process (this vol., i, 119).  
L. DE K.

**Extraction of Gases from Copper by a Chemical Method and the Estimation of Oxygen.** MARCEL GUICHARD (*Compt. rend.*, 1911, 153, 272—275).—Commercial copper is shown to contain sufficient dissolved oxygen to vitiate estimations of this gas carried out by its means. Fine copper wire previously heated at 600° in a vacuum for a long time should be used for the purpose. A specimen of copper liberated about twice its volume of gas when heated with iodine in a vacuum.  
W. O. W

**Detection of Mercury in Urine. II.** ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1911, 73, 401—406. Compare this vol., ii, 771).—The "end" solution is prepared in the manner previously described (this vol., ii, 771), and the mercury removed from it by leaving in the warmed solution for an hour or more two or three strips of copper foil about 0.1 mm. thick. These become grey when much mercury is present; they are removed, washed, and dried, care being taken to handle them only with forceps. They are next placed in a clean dry test-tube, which is moderately heated and allowed to cool; the foil is shaken out, a trace of iodine introduced, and the tube warmed until the iodine vapours fill two-thirds of it. The formation of the red mercuric iodide takes place slowly, but is very characteristic.

E. F. A.

**The Use of Sulphur Monochloride in the Determination and Analysis of the Rare Earth Minerals.** WILLIAM BROOKS HICKS (*J. Amer. Chem. Soc.*, 1911, 33, 1492—1496).—Fergusonite was completely decomposed by the action of the vapours of sulphur monochloride, not a trace of metallic acids remaining in the residue, and no rare earths being detected in the volatile portion. Eschynite and euxenite were also readily decomposed, whilst a picked sample of samarskite was decomposed to the extent of 98.78%.

In carrying out the decomposition, the minerals were placed in a porcelain boat in a combustion tube, which was heated while the vapours of sulphur monochloride were passed through it. The volatile chlorides of the metallic acids passed into the receiver, whilst the non-volatile chlorides or oxychlorides of the earth metals remained in the boat.

The principal advantages of this method of decomposition are the ease with which it takes place, the cheapness of the apparatus, and the separation of columbium, tantalum, titanium, and tungsten from the rare earths during the decomposition. The chief disadvantage is that the excess of sulphur monochloride is mixed with the volatile chlorides, but it may easily be overcome by allowing the mixture to pass into dilute nitric acid, and then removing the precipitated sulphur by adding excess of ammonium hydroxide and hydrogen sulphide.

In the non-volatile portions of the above minerals, search was made for scandium, but none was found. Fergusonite contained, however, 2—3% of thorium, whilst yttrium and thorium were found in eschynite.

T. S. P.

**A New Method for the Separation of Cerium.** CHARLES JAMES and L. A. PRATT (*J. Amer. Chem. Soc.*, 1911, 33, 1326—1330).—The authors have found that potassium bromate is capable of oxidising cerous nitrate in faintly acid or neutral solution, so that this element may be entirely separated from the other rare earths. The solution of the rare earth nitrates is boiled with potassium bromate in the presence of a lump of marble, the cerium being entirely precipitated as the basic ceric nitrate, with varying amounts of basic ceric bromate. When the operation is carefully conducted, the cerium thus obtained is free from the other rare earths. In working on a large scale with concentrated solutions, it is advisable to use a slight excess of the bromate, and to stop the action while about 1% of the cerium remains in the liquid. Under these conditions, a cerium product is obtained, which, after washing with a 5% ammonium nitrate solution, gives a pale straw-coloured oxide. A saturated solution of the nitrate of this material shows no trace of absorption spectrum when tested with a layer 20 cm. thick.

The above method may be employed for the gravimetric estimation of cerium. The cerium salt is precipitated twice, in each case until the mother liquor gives no test for cerium with hydrogen peroxide; the precipitate is washed with a 5% solution of ammonium nitrate. After the second precipitation the precipitate is dissolved in hydrochloric acid, the cerium precipitated as oxalate, and weighed as oxide.

Details are given of the application of the method to the purification of cerium on a large scale from the monazite earths which have been freed from thorium.

T. S. P.

**Analysis of Monazite Sands.** GABRIEL CHESNEAU (*Compt. rend.*, 1911, 153, 429—431).—The best methods hitherto published having proved unsatisfactory, the following process, which avoids difficulties caused by the sparing solubility of thorium phosphate in acid, was devised and found to give good results.

2.5 Grams of the sand are fused with 15 grams of fusion mixture until all glistening particles disappear. The mass is extracted with boiling 1% sodium hydroxide (solution *A*). The residue is treated with hot 5% hydrochloric acid (solution *B*), and the process repeated on the insoluble portion. The final residue ( $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ ) and solution *A* ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ ) are analysed in the usual way. Solution *B*, freed from lead and copper, is diluted until it contains exactly 4% of hydrogen chloride, then treated with 4 grams of crystallised oxalic acid for every 100 c.c., and allowed to remain for two days. The filtrate is examined in the usual way for  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , Fe, etc., and the oxalates of the rare earths calcined below  $500^\circ$ ; the oxides are dissolved in nitric acid, with addition of hydrogen peroxide if necessary. After evaporating to dryness and dissolving the residue in 150 c.c. of water, thorium is separated by double precipitation with hydrogen peroxide,

according to Wyruboff's method. The reagent should be free from phosphates, and is advantageously treated with a little ammonium nitrate to avoid formation of colloids. The filtrate is made up to 500 c.c., and the rare earths precipitated in 100 c.c. Cerium is estimated in another 100 c.c. by Job's method, for which details are given.

A monazite sand from Madagascar gave on analysis:  $\text{ThO}_2$ , 5.5;  $\text{CeO}_2$ , 22.6;  $\text{La}_2\text{O}_3$ ,  $\text{Di}_2\text{O}_3$ , 25.0;  $\text{Y}_2\text{O}_3$ , etc., 0.8;  $\text{ZrO}_2$ , 1.6;  $\text{Fe}_2\text{O}_3$ , 3.7;  $\text{Al}_2\text{O}_3$ , 0.8; Mn, trace;  $\text{MgO}$ , 0.4;  $\text{CaO}$ , 0.5;  $\text{P}_2\text{O}_5$ , 23.5;  $\text{SiO}_2$ , 8.8;  $\text{TiO}_2$ , 6.7; loss on ignition, 0.4. Total 100.3. W. O. W.

**Precipitation of Aluminium, Chromium, and Iron by Ammonium Nitrite.** ERIK SCHIRM (*Chem. Zeit.*, 1911, 35, 979—980).—Although sodium nitrite may be used in place of ammonium nitrite in the process described previously by the author (*Abstr.*, 1909, ii, 834), it has the disadvantage that alkalis cannot be estimated subsequently in the same portion of the sample. Manganese may be separated from iron by means of sodium nitrite, provided that a small quantity of ammonium sulphate be added to prevent precipitation of the manganese. A double precipitation is, however, recommended in this case. The manganese is then precipitated from the filtrate by means of ammonium persulphate. W. P. S.

**Estimation of Manganese as Manganous Oxide, Manganomanganic Oxide, and Manganese Sesquioxide.** PAUL N. RAIKOW and P. TISCHKOFF (*Chem. Zeit.*, 1911, 35, 1013—1015).—Manganese may be converted quantitatively into manganous oxide by heating the higher oxides in a rapid current of hydrogen, using a Rose's crucible. The higher oxides may be converted quantitatively into manganomanganic oxide by ignition in a slow current of carbon dioxide. Manganese may also be converted quantitatively into manganese sesquioxide by ignition of the oxides or the carbonate in a current of oxygen.

Manganous sulphate may be converted into the sesquioxide by heating alternately in a current of hydrogen and in air, and finally igniting in a current of oxygen. L. DE K.

**Ferric Sulphate as a Standard for Titrating Potassium Permanganate.** JAROSLAV MILBAUER and OTTO QUADRAT (*Zeitsch. anal. Chem.*, 1911, 50, 601—603).—One gram of pure ferric sulphate is dissolved in an Erlenmeyer flask in 25 c.c. of water and 10 c.c. of sulphuric acid, and, after adding a few granules of iron-free zinc, the whole is heated gently until everything has dissolved. An equal volume of water is added, and the solution titrated with permanganate.

Ferric sulphate is best prepared by boiling 10 grams of ferrous sulphate for about an hour with 100 c.c. of sulphuric acid. When cold, the bulk of the acid is poured off through a Gooch crucible, and the remainder removed by washing with alcohol, and then with anhydrous ether. Finally, the salt is dried in a water-oven to constant weight.

L. DE K.

**Volumetric Estimation of Ferric Salts with Permanganate after Reduction with Zinc.** ERICH MULLER and GUSTAV WEGELIN (*Zeitsch. anal. Chem.*, 1911, 50, 615—623).—When using pure zinc, or zinc in contact with platinum, for the reduction of ferric salts, it is necessary to wait until the zinc has completely dissolved, otherwise there will be a small quantity of iron deposited on the undissolved zinc. This inconvenience may be avoided by working as follows: 100 c.c. of the ferric iron solution (or a smaller volume diluted to 100 c.c.) are mixed with 5 c.c. of sulphuric acid and five to ten drops of *N*-copper sulphate. After adding three or four amalgamated zinc rods (5 cm. in length and 0.6 cm. in diameter), the solution is heated for about two hours at 100° in a current of carbon dioxide. The copper solution need only be added in the first experiment.

L. DE K.

**Precipitation of Iron with Hydrazine Hydrate.** ERIK SCHIRM (*Chem. Zeit.*, 1911, 35, 897).—The iron solution containing about 0.1 gram of iron is diluted to 250—300 c.c. If necessary, a few drops of hydrochloric acid and a little bromine are added, and the excess of the latter is boiled off. A large excess of ammonia is added, and then a few drops of hydrazine hydrate, which causes the precipitate to turn into a fine, granular black powder, which subsides rapidly and is free from sulphate. After washing and drying, it is ignited, finally over the blast, to constant weight. The filtrate may be used for estimating the sulphate.

Experiments to estimate iron in the presence of zinc by means of hydrazine hydrate are, as yet, unsuccessful.

L. DE K.

**Simplified Apparatus for Estimating Carbon in Iron** G. BUTZBACH and G. FENNER (*Chem. Zeit.*, 1911, 35, 917).—Two apparatus of the usual type are described and figured. In the first one the condenser is fixed to the flask containing the oxidising liquid by means of a rubber cork, which cannot be affected by spirting acid, and is rendered more effective by a water seal.

In the second one the flask is connected with the condensing tube by means of a ground joint. In both there is an absence of the usual side-tubes, thus rendering them less liable to breakage.

L. DE K.

**Employment of Combustion under Pressure in the Estimation of Carbon in Steels.** P. MAHLER and E. GOUTAL (*Compt. rend.*, 1911, 153, 549—551).—The sample of steel contained in a refractory crucible free from calcium carbonate is burnt in oxygen in a calorimetric bomb similar to those employed in determining the calorific power of coal, but having a capacity of about 1 litre. The carbon dioxide is absorbed by barium hydroxide, and estimated by titration. Results given by this method agree closely with those obtained by the copper chloride and combustion process. W. O. W.

**Rapid Estimation of Total Carbon [in Iron and Steel].** H. DE NOLLY (*Rev. de Métallurgie*, 1911, 8, 391—395).—The iron or

steel, in the form of fine drillings, is introduced into an asbestos capsule, supported in a litre flask of Jena glass, which is closed with a rubber stopper and supplied with oxygen under a pressure of 30 to 40 cm. of water. The flask contains a measured volume of a 0.4% solution of sodium hydroxide. The metal is ignited by passing a current of 10—15 amperes between a pair of electrodes. When combustion is complete, the flask is shaken to absorb carbon dioxide, and the solution is titrated with sulphuric acid (1 c.c. = 1 mg. of carbon) and phenolphthalein. White cast iron, ferro-silicon, and other brittle alloys are mixed with lead peroxide before ignition. Grey cast iron gives low results, owing to incomplete combustion of the graphite. C. H. D.

**Apparatus for the Estimation of Sulphur in Iron and Steel.** D. A. WENNMANN (*Chem. Zeit.*, 1911, 35, 863).—Diagrams are given of two apparatus made entirely of glass, so that all rubber connexions are avoided. T. S. P.

**Rapid Estimation of Ferric Oxide in Cement.** A. GOLUBINZEFF (*Chem. Zeit.*, 1911, 35, 961—962).—Two grams of the sample are placed in an Erlenmeyer flask, moistened with 10 c.c. of water, and allowed to remain for ten minutes, when another 75 c.c. of water and then, while shaking, 100 c.c. of *N*-hydrochloric acid are slowly added. The shaking is continued until the greater part of the cement has dissolved, when the solution of the remainder is effected by heating the liquid to boiling; the boiling is then continued for three to five minutes to expel any hydrogen sulphide. The solution is reduced by sulphur dioxide, the excess of which is then boiled off in a current of carbon dioxide. After some fifteen minutes, the exit tube is closed with a piece of rubber and clamp without interrupting the current of carbon dioxide, and the flask is cooled in cold water. The iron is titrated, as usual, with *N*/10-permanganate after adding 8—10 c.c. of a solution of manganese sulphate. L. DE K.

**Estimation of Ferrocyanides and Thiocyanates.** LÉON RONNET (*Ann. Chim. anal.*, 1911, 16, 336—337).—The solution is strongly acidified with hydrochloric acid, and a slight excess of a hot solution of ferric chloride is added. After heating for half an hour on the water-bath, the Prussian-blue is collected and washed with hot water. The filter and contents are then transferred to a graduated flask and treated with a sufficiency of 10% solution of potassium hydroxide, and, after being kept for twelve hours with frequent shaking, the whole is made up to a definite volume with water, and a known volume of the filtrate is then acidified with dilute sulphuric acid and titrated for ferrocyanide with *N*/10-permanganate as usual. One c.c. permanganate = 0.0422 gram of crystallised potassium ferrocyanide.

The filtrate from the Prussian-blue is made up to a definite volume, and an aliquot portion is heated on the water-bath with addition of a slight excess of sodium hydrogen sulphite. Solution of copper sulphate is then added in slight excess, and after half an hour the cuprous thiocyanate is collected and washed. The filter and contents

are then placed in a flask, and the precipitate is dissolved in dilute ammonia (1:2). The solution is acidified with dilute sulphuric acid, and, while still warm, titrated with *N*/10-permanganate; 1 c.c. = 0.001616 gram of potassium thiocyanate. L. DE K.

**Quantitative Separation with "Cupferron."** OSKAR BAUDISCH (*Chem. Zeit.*, 1911, 35, 913).—"Cupferron," so useful in the separation of iron from copper, not being readily procurable, the author recommends analysts to prepare it themselves. It is not explosive.

Sixty grams of nitrobenzene, 1000 c.c. of water, and 30 grams of ammonium chloride are well stirred, and to the white emulsion is added 80 grams of zinc dust in very small quantities, so that the temperature keeps between 16° and 18°. When the odour of nitrobenzene has completely disappeared, the solution is drawn off from the zinc hydroxide, and, after cooling to 0° by means of ice, the liquid is saturated with salt, which causes an abundant crystalline precipitate of phenylhydroxylamine. It may be observed that great care must be taken not to let this substance come in contact with the skin, as it is very poisonous. After draining and removing the mother liquor by means of filter paper, the compound is dissolved in 300—500 c.c. of ordinary ether, and after cooling the filtrate to 0°, a current of gaseous ammonia is passed for ten minutes and an excess of amyl nitrite is added. An abundant separation of nitrosylphenylhydroxylamine ammonium ("cupferron") takes place, which is drained, washed with ether, and then pressed between filter paper. It is advisable to place in the stock bottle a lump of ammonium carbonate.

L. DE K.

**The Separation of Iron and Vanadium by the Ether Method.** EUGEN DEISS and HANS LEYSAHT (*Chem. Zeit.*, 1911, 35, 869—871, 878—879).—Rothe's ether method (compare Blair, *Abstr.*, 1908, ii, 900) for the separation of iron from other elements cannot be used in its original form for the separation of iron and vanadium, since ether extracts appreciable quantities of vanadium from hydrochloric acid solutions, especially when the vanadium is in the quinquevalent condition. Solutions of quadrivalent vanadium do not give up any vanadium to ether so long as care is taken that reducing agents are present to prevent the oxidation of any vanadium by peroxide usually contained in ordinary ether. In ordinary practice it is not convenient to have such reducing agents present, since they would also reduce the ferric salts. Advantage is therefore taken of the fact that pervanadates are insoluble in ether. After the chief extraction has been carried out by Rothe's method, the ethereal extract, containing the ferric salt and some vanadium, is further shaken several times with ether-hydrochloric acid (hydrochloric acid, *D*=1.10, saturated with ether), to which a little hydrogen peroxide has been added. The hydrogen peroxide oxidises the vanadium to pervanadates, which then pass into the aqueous layer.

The many details necessary in carrying out the method are fully described. T. S. P.



**Estimation of Iron, Ammonia, and Nitrous Acid in Waters by means of the Autenrieth-Koenigsberger Colorimeter.** KARL SÜPFLE (*Arch. Hygiene*, 1911, 74, 176—184).—The above colorimeter is strongly recommended in water analysis.

Iron is estimated by the thiocyanate-ether process, ammonia by Nessler's reagent after removing alkaline earths, and nitrites are estimated by *m*-phenylenediamine and sulphuric acid; if necessary, the alkali earths and colouring matters are removed by adding a mixture of sodium carbonate and hydroxide. L. DE K.

**Rapid Detection of Elements Furnishing Sulphides Insoluble in Dilute Acids.** M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1911, [iv], 9, 812—814).—The mixed sulphides, precipitated by hydrogen sulphide from dilute acid solution, are treated with 25% hydrochloric acid, furnishing (1) a solution which may contain lead, antimony, tin, cadmium, and zinc, and (2) a residue, which may contain copper, molybdenum, arsenic, bismuth, mercury, gold, and platinum.

The solution is treated with ammonia, which precipitates the first three metals, and leaves cadmium and zinc in solution, where they can be detected by the usual tests. The precipitate, which may contain lead, antimony, and tin, is dissolved in hydrochloric acid, and these elements sought for by the usual tests.

The residue, insoluble in hydrochloric acid, is treated with nitric acid, which dissolves copper, molybdenum, arsenic, and bismuth, and leaves undissolved mercury, gold, and platinum, which are then obtained in solution with *aqua regia*. The elements are then sought for in these two solutions by the usual tests. The process is stated to give trustworthy qualitative results more rapidly than that in general use. T. A. H.

**Assay of Wolfram Concentrate.** H. W. HUTCHIN (*Analyst*, 1911, 36, 398—403).—A recapitulation of the four chief methods for the assay of commercial wolfram. In the *aqua regia* methods, the tungstic acid is finally obtained by ignition of ammonium tungstate or mercurous tungstate. In the soda digestion and fusion processes, the tungstic acid is finally obtained by ignition of mercurous tungstate.

All four methods seem to be very satisfactory; the old *aqua regia* ammonium tungstate method has, perhaps, most to commend it, as it allows of operating on 1 to 2 grams, whereas the other methods are limited to quantities of about 0.5 gram of the sample.

L. DE K.

**The Action of Salicylic Acid on the Metallic Acids.** JOHN HUGHES MULLER (*J. Amer. Chem. Soc.*, 1911, 33, 1506—1510).—Solutions of sodium or potassium columbate, tantalate, thorate, and zirconate are precipitated quantitatively by salicylic acid, whereas titanium is not so precipitated; this difference is used as the basis of a method for the quantitative separation of titanium from the other elements.

Alkali titanates give an intense yellow colour on the addition of salicylic acid ; the reaction is extremely delicate, and may be used for the colorimetric determination of this metal. The colour is destroyed by traces of hydrofluoric acid or of fluorides, and is affected by traces of iron. Zirconium gives a brownish tinge to the solution, which is also affected by large quantities of columbium. The effects of the rare earths, etc., are also described, and the colorimetric method is applied to the estimation of titanium in the presence of columbium, tantalum, or thorium.

Five % solutions of sodium tungstate or molybdate are not precipitated by salicylic acid, and the resulting solution gives no precipitate with ammonium hydroxide. Titanium is precipitated under such conditions, but the reaction cannot be used to separate titanium from tungsten and molybdenum.

T. S. P.

**The Detection of Small Quantities of Alcohol in Fermenting Liquids.** ALB. KLÖCKER (*Centr. Bakt. Par.*, 1911, ii, 31, 108—111).—In the systematic study of yeasts, one of the most important characteristics is the capacity of the organism to ferment different sugars. Where vigorous fermentation occurs, the usual qualitative tests may be employed, but even in cases where no apparent fermentation takes place, the author considers it necessary that actual tests should be made, and describes a modification of Pasteur's drop method, by means of which traces of alcohol may be detected.

Five c.c. of the liquid to be tested are poured into a test-tube 180 mm. long and 24 mm. wide. This is closed with a cork bearing a glass tube 180 cm. long and 3 mm. wide, which is allowed to protrude slightly on the lower side of the cork. The whole is then placed vertically over a flame with wire gauze, and is heated gently, care being taken that bumping does not occur. If alcohol is present, characteristic oily drops appear in the tube ; the lower the amount of alcohol, the higher being the point at which these drops occur.

It is claimed that by the use of this method, 0·002—0·001% of alcohol can be detected.

H. B. H.

**Estimation of both Phenol and *p*-Cresol in Urine.** MAX SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1911, 34, 462—472. Compare this vol., ii, 72).—The urine, after being made alkaline with sodium hydroxide, is evaporated to 1/5th of its bulk, acidified with sulphuric acid, and then distilled in steam. To separate volatile acids from phenols, the distillate is made alkaline with sodium hydrogen carbonate, and distilled in steam in a current of carbon dioxide. The reducing substances are separated then by Neuberg's method by means of lead acetate and sodium hydroxide, and then, after distillation of these substances, the phenols are distilled off after acidification with sulphuric acid. The phenol and cresol are then estimated by the method already given by the authors, which they find preferable to that of Kossel and Penny. The analyses of mixed urines from several individuals showed that 1·5 litres contained 0·0260 gram of *p*-cresol and 0·0186 gram of phenol ; 58·1% of the total phenols consisted

therefore of *p*-cresol. The details are given of the experiments on which the analytical method is founded. S. B. S.

**Estimation of Phenols in the Urine of Oxen.** PAUL LIECHTI and W. MOOSER (*Zeitsch. physiol. Chem.*, 1911, 73, 365—370. Compare Neuberg and Hildesheimer, Abstr., 1910, ii, 1116).—Polemical. The supposed formation of furfuraldehyde on distillation of herbivorous urine with phosphoric acid, derived from dextrose, pentose, or paired glycuronic acid, is shown not to take place. The Kossler-Penny process advocated by Neuberg and Hildesheimer (*loc. cit.*) leads to far larger errors than any neglect of the furfuraldehyde formed. The substitution of phosphoric acid for sulphuric acid in the distillation prevents the formation of urogon, which otherwise fixes iodine; further aldehydes present are not hydrolysed in such a way as to affect the estimation of the phenols. E. F. A.

**Estimation of Volatile Acids in Wine.** KARL WINDISCH and THEODOR ROETTGEN (*Zeitsch. Nahr. Genussm.*, 1911, 22, 155—170).—It is recommended that 50 c.c. of the wine should be distilled in a current of steam until 200 c.c. of distillate have been collected; if the distillation is continued beyond this, considerable quantities of lactic acid are found in the distillate. When the wine contains more than 0.2 gram of volatile acids per 100 c.c., it should be diluted with an equal volume of water, and 50 c.c. of the mixture taken for the estimation. The volume of the steam must be so regulated that the wine is first evaporated to 25 c.c. and maintained at this volume until the end of the distillation. The time taken for the distillation is about thirty minutes; the steam should be under as low a pressure as possible, and it is advisable to employ a still-head filled with glass beads in order to reduce the distillation of the lactic acid to a minimum. W. P. S.

**Employment of the Electrometric Method for the Estimation of the Acidity of Tan Liquors.** II. JOSEPH T. WOOD, HENRY J. S. SAND, and DOUGLAS J. LAW (*J. Soc. Chem. Ind.*, 1911, 30, 872—876).—A hydrogen electrode is described for use in the electrometric method of estimating the acidity of tan liquors (this vol., ii, 233); slight improvements in the general form of the apparatus are proposed, and experimental details and results are recorded. W. P. S.

**Analysis of Liquids containing a Large Quantity of Tartaric Acid and Small Amounts of Glycerol and Tannin.** G. HINARD (*Ann. Falsif.*, 1911, 4, 391—397).—Having experienced certain difficulties in the analysis of solutions containing about 100 grams of tartaric acid, 10 grams of glycerol, and 3 grams of glycerol per litre, the author gives the following methods for the estimation of these constituents and of the total solids of the solution. The total solids may be estimated by drying 5 c.c. of the solution on pumice-stone over sulphuric acid and under as low a pressure as possible; at the end of twenty-four hours, the temperature of the desiccator is raised to 50°, and the drying is continued over phosphoric

oxide to constant weight. For the estimation of the glycerol, 100 c.c. of the solution are treated with sufficient potassium hydroxide to convert the tartaric acid into potassium hydrogen tartrate; the latter is removed by filtration, and the filtrate is evaporated at a low temperature after the addition of freshly prepared lead hydroxide. The residue is extracted with hot alcohol, the solution filtered, excess of lead is precipitated as carbonate, and an equal volume of ether is added, together with a few grams of potassium carbonate. The solution is then filtered, evaporated, and the residue dried under reduced pressure. The tartaric acid may be estimated by the methods used in wine analysis, and the tannin is estimated iodometrically.

W. P. S.

**Estimation of Milk Fat by Count of the Fat Globules.** H. P. T. OERUM (*Biochem. Zeitsch.*, 1911, 35, 18—28).—The relationship between the number of fat globules in a given measure, the transparency of the milk (the experimental method for determining which is described), and the fat content is mathematically worked out. The conclusion is drawn that each observer must obtain his own formula for each kind of milk, and the method has, therefore, no immediate practical value.

S. B. S.

**Assay of Chloral.** L. BOURDET (*J. Pharm. Chim.*, 1911, [vii], 4, 18).—The author suggests that in assaying chloral by the method prescribed in the French Codex, (1) distilled water, freed from carbonic acid, should be used; (2) a control experiment with water and alkali alone should be made; (3) *N*/2-alkali should be substituted for *N*-alkali, and (4) the time of contact of the alkali with the chloral should be reduced to fifteen minutes.

T. A. H.

**Ulex's Process for the Estimation of Nicotine in Tobacco Extracts and Nicotine Salts.** JULES ESSNER (*Ann. Chim. anal.*, 1911, 16, 339—341).—A recapitulation of Ulex's process (treatment of the extract with a mixture composed of aqueous sodium hydroxide, calcium oxide, and plaster of Paris, removal of ammonia fumes in a desiccator over sulphuric acid, distillation with water, and titration of the nicotine with standard acid), which the author strongly recommends for technical purposes. The author carries out the distillation and titration as follows: The mass is placed in a 3-litre distillation flask containing  $2\frac{1}{2}$  litres of boiled water, 10 grams of sodium hydroxide and 10 grams of paraffin (to prevent frothing) are added, and the whole is submitted to distillation. Six portions of 1000, 500, 200, 100, 100, and 100 c.c. respectively are collected and titrated separately with *N*/2-hydrochloric acid, using delicate litmus solution as indicator; 1 c.c. of acid = 0.081 gram of nicotine.

L. DE K.

**Comparative Studies on the Nicotine Estimations in Tobacco Extracts.** JULIUS TÓTH (*Chem. Zeit.*, 1911, 35, 926—927).—At the author's suggestion, J. KRAMPERA analysed a sample of tobacco extract by the methods of Kissling, Ulex, Degrazia, and Tóth,

and the results are given in a table; in a second table are given the results of analyses made by the methods of Kissling, Koenig, Tóth, and the modified process of the latter. This consists in substituting xylene for toluene in the extraction of the nicotine; the results obtained by titration and polarisation are very concordant.

On the whole, the author has reason to prefer his own modified process.

L. DE K.

**Estimation of Quinine as Acid Citrate in Certain Organic Liquids.** THOMAS COCKBURN and J. W. BLACK (*Analyst*, 1911, 36, 396—398).—A slight modification of Nishi's process for the estimation of quinine in urine (Abstr., 1909, ii, 710). Two hundred and fifty c.c. of urine are rendered alkaline with concentrated aqueous sodium hydroxide and extracted three times with ether. The ethereal extracts are washed with small quantities of water, evaporated, the residue dried and dissolved in 20 c.c. of anhydrous ether, and the solution is filtered into a weighed flask with which has also been weighed a small asbestos filter tube, and the undissolved matter is washed with small quantities of ether. The quinine is now precipitated by adding 10 c.c. of a saturated ethereal solution of citric acid, and the closed flask is left for twenty-four hours. The ether is then poured off through the filter-tube, and the deposit is washed thrice in succession with 10 c.c. of ether, D 0.720. The tube is then placed in the flask, and the whole is dried, first gently, finally at 100°, and re-weighed; 100 parts of the acid citrate = 62.79 parts of quinine.

The process may be used in the presence of caffeine, but not of other cinchona alkaloids.

L. DE K.

**Separation of Urobilin by means of Talc and its Detection.** C. CARREZ (*Ann. Chim. anal.*, 1911, 16, 337—339).—The urine is defecated by mixing 45 c.c. with 30 c.c. of Denigès' mercury reagent, and to 30 c.c. of the clear filtrate is added 1 gram of talc, which on shaking removes all the urobilin; the talc is then at once collected on a filter and washed with water. In order to prove the presence of the urobilin, the talc is treated on the filter with 5 or 10 c.c. of Oliveri's reagent (zinc chloride 10 grams, ammonia 30 grams, strong alcohol 80 grams, ethyl acetate 20 grams), when at once a filtrate is obtained presenting a beautiful green fluorescence and exhibiting in the spectro-scope very neatly the band  $\gamma$ .

Or the talc may be treated with 10 c.c. of alcohol containing 5% of hydrochloric acid. To the filtrate is then added 5—6 c.c. of chloroform and 100—150 c.c. of water, and the whole is well shaken. The chloroform layer separates readily, and is then removed and filtered through a small filter moistened with chloroform. On adding an alcoholic solution of zinc acetate (1:1000), a green fluorescence is gradually formed, and the band  $\gamma$  is more distinct than before.

L. DE K.

**Estimation of Amino-groups in Amino compounds and in Urine and a Method for the Analysis of Proteins.** DONALD D. VAN SLYKE (*Ber.*, 1911, 44, 1684—1692; *J. Biol. Chem.*, 1911, 10, 15—55. Compare this vol., ii, 164, 779, 780).—Glycine, cystine, and

guanosine give high values when treated by the method already described.

Carbamide reacts slowly with the nitrous acid solution, and this reaction must be allowed for in estimating the amino-acid nitrogen in urine. After removal of ammonia from the urine made alkaline with sodium hydroxide solution, two estimations are made of the amino-acid nitrogen, one after six minutes and the other after the mixture has been left for twelve minutes. The difference between the two gives the error due to the reaction of the carbamide, and can be subtracted from the result given by the six minute determination.

Full details are given of a somewhat revised scheme for the analysis of proteins by the method of hydrolysis and nitrogen determinations. The following substances have been treated in this way: gliadin, edestin, hair, gelatin, fibrin, hæmocyannin, hæmoglobin, and the results are expressed in percentages of ammonia nitrogen, melanin nitrogen, cystine-, arginine-, histidine-, lysine-nitrogen, amino-nitrogen of filtrate, and non-amino-nitrogen of filtrate. Gelatin and hæmoglobin did not give any cystine nitrogen. J. J. S.

**An Inner Anhydride Reaction of Albumin.** BRUNO BARDECK (*Chem. Zeit.*, 1911, 35, 634).—The author's iodoform process (this vol., ii, 826) when applied to albumins shows that these give very intense anhydride reactions. L. DE K.

**Rapid Gravimetric Estimation of Urinary Albumin.** E. SIMONOT (*Bull. Soc. chim.*, 1911, [iv], 9, 839—842).—This method, which depends on the coagulation of the albumin by metaphosphoric acid, is stated to afford complete precipitation of the albumin in a form in which it can be easily and rapidly filtered, and washed (compare Denigès, *Abstr.*, 1893, ii, 248).

Five grams of sodium metaphosphate are dissolved in cold water, and made up to 100 c.c., or 5·70% grams of the metaphosphate may be dissolved by boiling in water during five minutes and made up to 100 c.c. as suggested by Denigès (*Chim. Anal.*, 3rd Edit., 1907, p. 1011). A preliminary trial having shown that the urine contains more than 0·5 gram albumin per litre, enough to yield about 10 grams is taken, filtered, made up to 100 c.c. if necessary, heated on the water-bath during ten minutes (during fifteen minutes if the quantity is 200 c.c.), and then for every 100 c.c. of liquid, 5 c.c. of the metaphosphate solution and 1 c.c. of hydrochloric acid are added and the heating continued during five to ten minutes. The coagulum is filtered on a dry tared filter and washed with boiling water until free from hydrochloric acid, and then twice with alcohol and once with ether. As much liquid as possible is removed by gentle pressure, and the coagulum dried at 110—120°. The weight, re-calculated for 1 litre of urine and multiplied by 0·88, gives the amount of albumin per litre in the urine examined.

T. A. H.

**Estimation of Lecithin.** C. VIRCHOW (*Chem. Zeit.*, 1911, 35, 913—914).—The author has slightly modified his process. One gram of the substance is boiled three times in succession with 10 c.c. of

absolute alcohol, and the filtrate and washings, measuring about 50 or 60 c.c., are distilled off. After removing the last traces of alcohol by blowing, the weighed residue is dissolved in 10 c.c. of absolute ether, which is then poured through an asbestos filter tube; the residue is then washed three times with ether.

The ether is distilled off, and the weighed residue treated with 3—4 c.c. of fuming nitric acid; the solution is transferred to a platinum dish, and the flask rinsed three times in succession with 2 c.c. of fuming nitric acid. After evaporating the acid on the water-bath, the residue is mixed with 1 gram of dry sodium carbonate, using a platinum spatula. Five grams of the usual potassium nitrate-sodium carbonate mixture are now added, and the whole is heated to fusion for four to five minutes. The fusion contains the phosphorus of the lecithin as phosphoric acid, which is then estimated by the usual magnesia process.

L. DE K.

**A Method for Ash Analysis.** KARL STOLTE (*Biochem. Zeitsch.*, 1911, 35, 104—107).—The essential feature of the method consists in ashing the dried organic substance in a platinum basin placed inside a larger porcelain basin but kept from direct contact with it by pieces of porous plate, or an inverted crucible lid.

S. B. S.

**A New Colour Reagent for Callose.** M. TSVERT (*Compt. rend.*, 1911, 153, 503—505).—The reagents hitherto in use for callose are slow in action; the following one is very rapid. A 1% aqueous solution of resorcinol, containing 0.1% of concentrated ammonia, is allowed to remain for several days exposed to the air. It gradually undergoes oxidation, and gives rise to a blue substance apparently identical with Würster's resorcinol-blue, which the author calls *resoblue*.

Resoblue does not stain cellulose, but in thirty to sixty seconds it imparts a deep blue colour to callose. It can also be mixed with other stains to give double reactions; thus the mixture with Congo-red is stable, and colours callose blue and cellulose red. Other mixtures are also suggested.

E. J. R.

**Use of Nickel Hydroxide in Tannin Estimation.** PURAN SINGH (*J. Soc. Chem. Ind.*, 1911, 30, 936—937).—Results of experiments carried out by the author indicate that nickel hydroxide may be employed as a substitute for hide-powder in the analysis of tanning materials. The figures obtained were in fair agreement with those found when hide-powder was used.

W. P. S.

**Application of the Bromo-derivative Methods for the Assay of Vulcanised Rubber Wares.** WERNER ESCH (*Chem. Zeit.*, 1911, 35, 971—972).—The process in use is based on the following assumptions: (1) 136 parts of rubber hydrocarbons absorb 319.7 parts of bromine or 64 parts of sulphur; (2) if 136 parts of hydrocarbons have already absorbed 32 parts of sulphur (in consequence of vulcanisation), only 159.85 parts of bromine can be taken up; (3) the sulphur absorbed is not acted on by bromine solutions; (4) if from the



total weight is deducted the combined sulphur and the bromine absorbed, the value of the rubber substance present is obtained ; (5) from 64 parts of combined sulphur or from 319.7 parts of bromine absorbed, the presence of 136 parts of rubber hydrocarbons may be deduced.

According to the author's experiments, these assumptions cannot be entertained, and the process is therefore quite untrustworthy.

I. DE K.

**Estimation of the Specific Gravity of very small Quantities of Milk.** ALOIS KREIDL and EMIL LENK (*Biochem. Zeitsch.*, 1911, 35, 166—168).—As fat is not extracted from milk by simple mixture with a lipid solvent, the specific gravity can be determined by dropping the milk into mixtures, such as benzene-chloroform, benzene-carbon tetrachloride, etc., and finding the specific gravity of the mixture in which the milk neither sinks nor floats.

S. B. S.

**A New Modification of the Forensic Chemical Test for Blood.** OTTO VON FURTH (*Zeitsch. angew. Chem.*, 1911, 24, 1625—1628).—In testing for blood, the author recommends a combination of Leer's pyridine test with the leucomalachite-green test (Adler, Abstr., 1904, ii, 459). The object to be tested is boiled for some minutes with a few drops of 50% potassium hydroxide to which a few drops of alcohol have been added. After cooling, the liquid is extracted with pyridine. The pyridine layer is separated, and again shaken with concentrated potassium hydroxide, after which about 1 c.c. of the solution is run on to a filter paper laid on a glass plate. This is then tested with the leucomalachite-green solution, to which has previously been added 1% of hydrogen peroxide.

A full discussion of the sensitiveness of the test and of any errors which may occur is given.

T. S. P.

**Meyer's Reagent for the Detection of Blood.** A. SARTORY (*Compt. rend.*, 1911, 152, 131—133).—The red coloration produced by blood in presence of hydrogen peroxide with phenolphthalein previously reduced by zinc, is also given by alkali hydrogen carbonates. The test cannot therefore be taken as specific for blood, and should only be used as a confirmatory test.

W. J. Y.

**Estimation of Gelatin.** W. GREIFENHAGEN, J. KÖNIG, and A. SCHOLL (*Biochem. Zeitsch.*, 1911, 35, 217—227).—Beckmann's formaldehyde method is of little practical value. Precipitation by Nessler's reagent by Vamvaka's method brings down all the gelatin, but it also precipitates proteoses. Although trichloroacetic acid (Obermayer's method) only produces a turbidity with dilute solutions of gelatin, it does not completely precipitate proteoses, and this reagent therefore cannot be employed for separating these substances from gelatin. Mercuric chloride solution does not produce a quantitative separation, but if it precipitates the same amount of nitrogenous matter as zinc sulphate, the conclusion may be drawn that gelatin is not present.

Mercuric iodide can also be employed as a precipitant. If the solution is first precipitated by zinc sulphate, the precipitate redissolved, and mercuric iodide in acetone or alcohol added (with precautions described in detail by the authors) and a precipitate is then produced which contains a large proportion of the nitrogenous matter which was precipitated by the zinc sulphate, then it may be deduced that gelatin is present. A satisfactory method for separating gelatin from proteoses does not exist.

S. B. S.

**Analyses of Liquorice Juices.** L. GADOIS and J. GADOIS (*Bull. Soc. chim.*, 1911, [iv], 9, 741—743).—The analyses of liquorice juices by different methods having furnished discrepant results, the following analytical method was adopted: The moisture was estimated by drying at 100°, insoluble matter by two extractions with cold water for twenty-four hours, and the ash by ignition. The glycyrrhizin was determined by precipitating the resinous matter from aqueous solution with alcohol, concentrating the filtrate, and precipitating with hydrochloric acid in a weighed beaker, the precipitate being washed with water, treated with ammonia, and the ammonium derivative dried at 100°.

W. G.

**A New Method for the Detection of Salvarsan (Diaminodihydroxyarsenobenzene).** J. ABELIN (*Münch. Med. Woch.*, 1911, 19. A Reprint).—A very little of the salvarsan is dissolved in 2—3 c.c. of water, and the yellow solution is decolorised by addition of 3—4 drops of dilute hydrochloric acid. After cooling the solution, 3—4 drops of a 0.5% solution of sodium nitrite are added, when a diazo-compound is formed, showing a vivid yellowish-green fluorescence. The liquid is now added, drop by drop, to a 10% solution of resorcinol, to which an excess of sodium carbonate has been added, when a beautiful red colouring matter will be formed; care must be taken that the liquid remains alkaline.

When applying the process to urines, 7—8 c.c. of the sample are acidified with 5—8 drops of dilute hydrochloric acid, and when cold, 3—4 drops of the above sodium nitrite solution are added. A few drops of the liquid are then added to 5 c.c. of the alkaline resorcinol solution, or the ring test may be applied successfully.

Atoxyl, treated as above, yields an orange colouring matter.

L. DE K.

**Pyro-Analyses of Drugs.** LEOPOLD ROSENTHALER (*Ber. Deut. pharm. Ges.*, 1911, 31, 338—346).—A microscopical and chemical investigation of crystalline sublimates obtained in vacuum from a number of drugs. Probably it would be better still to subject their extracts to the sublimation process. For the micro-illustrations and properties of the various sublimates, the original paper should be consulted.

The following drugs were examined: *Cortex chinæ*, *Folia uvæ ursi*, *Cortex frangulæ*, *Cortex cascaræ sagradæ*, *Rhizoma rhei*, *Gallæ*, *Rhizoma hydrastis*, *Opium*, *Cubebæ*, *Semen calabar*, *Piper nigrum*, and *Fructus anisi*.

L. DE K.