

## Analytical Chemistry.

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**The Application of the Ionic Theory in Analytical Chemistry.** O. HACKL (*Jahrb. K. K. Geol. Reichsanstalt*, 1913, **62**, 613—648).—A criticism of a statement by W. Ostwald ("Die wissenschaftlichen Grundlagen der Analytischen Chemie") on this subject.

F. M. G. M.

**Burette with Automatic Setting of the Zero Point.** P. HAERTL (*Zeitsch. anal. Chem.*, 1913, **52**, 759—760).—An improved automatic burette, which can be affixed to any bottle filled with stock liquid, is described and figured.

L. DE K.

**A New Still-head with Dropping Funnel.** OTTO RAMMSTEDT (*Zeitsch. angew. Chem.*, 1913, **26**, 640).—For estimations which involve the addition of a reagent immediately preceding or during a distillation, a device is described in which a graduated dropping funnel is fused to the stem of a still-head of the type commonly used for ammonia distillations.

J. C. W.

**New Apparatus for the Rapid Estimation of Water in Foods and Fodder.** ARTUR FORNET (*Chem. Zeit.*, 1913, **37**, 1400).—The author has carried out a series of determinations of the water content of flour and bran (1) at 100°, (2) at 105°, (3) in a vacuum, and (4) at 125°. The results show considerable variation among themselves. After fourteen to sixteen hours, a further loss of water does not appear to occur, but, on continuing desiccation at 125°, the products treated according to (1) and (2) were further dehydrated, the loss ultimately attaining the same value as in (3) or (4). The author is therefore led to the conclusion that the generally adopted methods of determining moisture in grain, bran, and flour yield too low results. The latter are, however, satisfactory if heating takes place during four hours at 105° in a stream of air.

The author has further investigated the possibility of desiccation at a higher temperature; this is found to be complete in about ten minutes at 180°, and can be effected without decomposition of the substance provided that the duration of heating, determined for any class of substance by comparison of the loss obtained by this method with the analytically determined amount of moisture, is not exceeded. The necessary apparatus consists of a drying oven which can be rapidly heated to and easily maintained at 160°, and a lever arrangement by which the substance can be weighed whilst hot, and which is so calibrated that the percentage of moisture can be read directly.

The author replies to some criticisms by Parow (*Chem. Zeit.*, 1913, **37**, 345), who, using the above method, found too low values for the percentage moisture in starch. The explanation is to be

found in the fact that the method yields only conventional results, and therefore, if standardised against starch at 105°, naturally yields results which are low when compared with the loss observed at 120° if the duration of heating is kept constant. H. W.

**The Estimation of Traces of Chlorides in Water.** MAURICE LOMBARD (*Bull. Soc. chim.*, 1913, [iv], 13, 1006—1011).—In estimating traces of chlorides in natural waters by titration with *N*/100-silver nitrate solution, using potassium chromate as an indicator, it is necessary to take certain precautions. A known volume of the water (150—200 c.c.) must be boiled until all the calcium hydrogen carbonate is decomposed, then it is allowed to cool, made up to the original volume, left to settle, decanted, and 100 c.c. of the clear liquid titrated with the silver nitrate. The end-point is determined by colorimetric test against the end-point, made with 100 c.c. of a standard solution containing 5 mg. of sodium chloride per litre. Hydrogen sulphide in water is destroyed by boiling with a slight excess of nitric acid, which is finally removed by the addition of calcium carbonate. Ammonia can be similarly neutralised. W. G.

**Estimation of Periodate in Presence of Iodate and Iodide** ERICH MÜLLER and GUSTAV WEGELIN (*Zeitsch. anal. Chem.*, 1913, 52 755—759).—To 20 c.c. of the solution (about *N*/10-strength) are added 20 c.c. of a saturated solution of borax containing 0.5 gram of free boric acid, 2 grams of potassium iodide are added, and the liberated iodine, which represents one-quarter of the periodate oxygen, is titrated with *N*/10-arsenious acid. Dilute sulphuric acid is now added until the liquid is acid to Congo-paper, and after again neutralising by means of a saturated solution of borax, the iodine liberated is again titrated. If in the first titration *a* c.c. of *N*/10-arsenic were used, and *b* c.c. in the second,  $4a$  c.c. will represent the periodate, and  $a + b - 4a = b - 3a$  the iodate oxygen. L. DE K.

**Estimation of Fluorine in Zinc Ores.** LEOPOLD SCHNEIDER (*Österr. Zeitsch. Berg. Hüttenwesen*, 1913, 16, 365—367).—The estimation of fluorine in minerals by distilling with concentrated sulphuric acid over quartz and weighing the orthosilicic acid ( $\text{Si}(\text{OH})_4$ ) subsequently separated by means of water (Bein, A., 1888, 527) is considered unsatisfactory; and a method is now described in which the fluorine is precipitated and weighed as calcium fluoride in the presence of silica, and the latter afterwards removed by treatment with hydrofluoric acid. F. M. G. M.

**A Simple Method of Calibrating the Differential Blood-gas Apparatus.** PAUL HOFFMANN (*J. Physiol.*, 1913, 47. 272—274).—A simpler method than that of Barcroft is described, and gives equally good results. W. D. H.

**Determination of Alkali Sulphides.** DOUGLAS McCANDLISH and JOHN ARTHUR WILSON (*Collegium*, 1913, 80—84).—A discussion

of the method advocated by Blockey and Mehd (A., 1912, ii, 600) for the estimation of sulphur in lime liquors, with a description of modifications which are considered to give more satisfactory results.

F. M. G. M.

**Source of Error in Estimating Nitrogen in Urine by Kjeldahl's Method.** O. VON SPINDLER (*Chem. Zentr.*, 1913, ii, 1340; from *Schweiz. Woch. Chem. Pharm.*, 1913, 51, 517—521).—Under ordinary conditions of feeding, urine almost always contains nitrates, and their presence affects the results in the estimation of the total nitrogen in the urine by Kjeldahl's method. Loss of free nitrogen takes place, but is not proportional to the quantity of nitrate present. The loss may be diminished by taking care that not more than 0.01 gram of nitric acid is present in the quantity of urine used for the estimation, and that the volume of the digestion mixture is not too small at the commencement of the operation.

W. P. S.

**Decomposition of Organic Substances by Kjeldahl's Method and the Estimation of Nitrogen in Barley.** KURT BUNGE (*Pharm. Zentr.-h.*, 1913, 54, 1127—1128).—The following procedure is recommended, as it allows a relatively large quantity of the sample to be taken for the estimation. Ten grams of the unground barley grains are heated for thirty minutes with 60 c.c. of sulphuric acid, and about 1.5 grams of mercury in a round-bottom, 500 c.c. flask. To the dark-coloured solution are then added 25 grams of potassium sulphate, and the heating is continued until a clear solution is obtained; the solution is now cooled, diluted to 500 c.c. with water, and the ammonia is estimated in an aliquot portion.

W. P. S.

**Ammonia Absorption Apparatus for Nitrogen Estimations.** HERBERT LICKFETT (*Zeitsch. angew. Chem.*, 1913, 26, 688).—The absorption flask has a wide neck, and is fitted with a rubber stopper, through which pass (1) the tube from the condenser and (2) a tube with two glass bulbs; this tube may be adjusted, so that the end just dips below the surface of the standard acid in the flask.

W. H. G.

**Detection of Nitric Acid (Nitrates) in Milk.** R. BARTH (*Zeitsch. Nahr. Genussm.*, 1913, 26, 339—341).—The formaldehyde-sulphuric acid test is recommended. Ten c.c. of the milk are mixed with 5 drops of dilute formaldehyde solution (10 drops of 40% formaldehyde in 250 c.c. of water), and the mixture is poured on the surface of 5 c.c. of sulphuric acid, D 1.71, contained in a test-tube. A blue ring appears at the junction of the two liquids when the milk contains not less than 0.5 mg. of nitric acid per litre. Care must be taken to see that the sulphuric acid, water, etc., used in the test are free from nitric acid.

W. P. S.

**Estimation of Phosphorus in Fertilisers and Fodders.** C. DUSSERRE and P. CHAVAN (*Chem. Zentr.*, 1913, ii, 1333—1334; from *Mitt. Lebensmittelunters. Hyg.*, 1913, 4, 261—267).—Molinari's

modification of Pemberton's method, in which Petermann's solution is added to the phosphate solution, yields trustworthy results in the case of superphosphates, but the results are too low with Thomas slag and bone-meal when sulphuric acid solutions of these substances are used for the estimation. This error may be avoided by adding ammonium sulphate to the molybdic acid reagent in place of the usual ammonium nitrate. The molybdic acid reagent is prepared by adding a solution of 25 grams of ammonium sulphate in 400 c.c. of nitric acid, D 1.12, to 75 grams of ammonium molybdate dissolved in 500 c.c. of water, and diluting the mixture to 1 litre. Results of analyses are given showing the distribution of phosphorus in hay (as lecithin, inorganic, and nuclein compounds). The lecithin-phosphoric acid was estimated by extracting the hay repeatedly with boiling alcohol, then with ether, evaporating the solutions, and oxidising the residues with a mixture of sulphuric and nitric acids. The hay was next extracted with cold 1% hydrochloric acid to obtain the inorganic phosphates in solution, and the nuclein-phosphoric acid was estimated by digesting the hay subsequently with sulphuric and nitric acids; in all these estimations, the phosphoric was, finally, precipitated with molybdic acid reagent.

W. P. S.

**Source of Error in the Precipitation of Ammonium Magnesium Phosphate in the Presence of Ammonium Citrate.** ALFREDO QUARTAROLI (*Chem. Zentr.*, 1913, ii, 539; from *Staz. sperim. agrar. ital.*, 1913, 46, 322—328).—Results of experiments are given in tabular form showing that the amount of phosphoric anhydride, precipitated as ammonium magnesium phosphate in the presence of ammonium citrate, diminishes rapidly as the quantities of ferric and aluminium compounds in the solution increase.

W. P. S.

**Reactions of Boric Acid and Methyl Alcohol.** ERNST PIESZCZEK (*Pharm. Zeit.*, 1913, 58, 850—851).—A mixture of borax and methyl alcohol yields a green-coloured flame when ignited, and the addition of sulphuric acid is unnecessary. Since ethyl alcohol, acetaldehyde, and acetone do not yield a green flame when burnt in the presence of borax unless a mineral acid is also present, the test may be used, conversely, for the detection of methyl alcohol in ethyl alcohol. The presence of 5% of methyl alcohol may be detected by this means.

W. P. S.

**Titration of Boric Acid.** EDMUND B. R. PRIDEAUX (*Zeitsch. anorg. Chem.*, 1913, 83, 362—368).—A comparison of the behaviour of various indicators with the neutralisation curve of boric acid suggests the possibility of titrating boric acid without the addition of glycerol or mannitol. The neutralisation curve has been determined from the results of Schmidt and Finger (*A.*, 1908, ii, 802) and Sørensen (*A.*, 1909, i, 861; 1910, i, 147). The best indicator is tropaeolin-O (sodium *p*-benzeneazoresorcinolsulphonate), using 0.5 c.c. of a 0.04% solution for a total volume of about 68 c.c. The

accuracy of the titration in concentrated and dilute solutions, and also with the addition of sodium chloride, is in agreement with that calculated theoretically. The method may be used with an accuracy of  $\pm 1\%$ .  
C. H. D.

**Absorbing Apparatus for the Estimation of Carbon in Organic Analyses.** HENRI VIGREUX (*Bull. Soc. chim.*, 1913, [iv], 13, 955—958).—The gas produced in the combustion passes through a straight tube to the bottom of the first washer, where it passes into an outer tube, the inner surface of which is spirally furrowed. The gas passes along the furrow, and escapes by a minute hole at the top leading into the second washer, which is of the usual pear-shaped bubble-counter pattern. The progress of the combustion can be watched easily by comparing the sizes of the bubbles of gas in the two washers. A modified form of the apparatus is also made for the estimation of iodine or chlorine, or of oxidising agents liberating chlorine by the action of hydrochloric acid. Figures are provided in the original.  
T. A. H.

**Tube for the Absorption of Water in Elementary Analysis.** JEAN NIVIÈRE (*Bull. Soc. chim.*, 1913, [iv], 13, 958—959).—The apparatus which is figured in the original consists of a tube closed at the bottom and having a constriction about one-quarter of its length from the bottom, and two narrow side-arms near the top. The side-arm used as an inlet is prolonged inside to the bottom of the tube. The latter is filled nearly to the constriction with sulphuric acid, and above that with pumice stone previously soaked in sulphuric acid.  
T. A. H.

**Apparatus for the Extraction of Carbon Monoxide from Blood.** MAURICE NICLOUX (*Bull. Soc. chim.*, 1913, [iv], 13, 947—952).—The apparatus consists essentially of a long-necked flask, the neck of which is jacketed to carry a current of cold water. The mouth of the flask is closed by a hollow ground glass stopper carrying a T-piece of special form, the two outer limbs of which are provided with stoppers, and terminate in funnels of special form, by means of which the flask can be (a) exhausted, and (b) supplied with the blood under examination. The blood is run into dilute phosphoric acid in the flask, and the gas liberated can, by appropriate manipulation, be collected and withdrawn for examination. The apparatus is figured in the original, and results obtained by its use are quoted.  
T. A. H.

**Application of the Electrical Conductivity to the Investigation of Natural Waters.** ANTONY G. DOROSCHEVSKI and S. V. DVORSHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 1489—1528).—The authors have investigated the relation of the electrical conductivity to the amount of dry residue in the case of a number of salt solutions and of natural waters. With salt solutions, especially those of calcium and, to a greater extent, magnesium salts, drying of the residue for two hours at  $110^\circ$  gives

results very considerably in excess of the true values, owing to the retention of water of crystallisation. When, however, the water is evaporated, together with a definite proportion of standard sodium carbonate solution sufficient to convert the calcium and magnesium salts into carbonates, the corrected experimental results never exceed the actual values by more than 1—2%; at the same time, almost identical results are then obtained at 110° and 103°. With artificial mixed salt solutions resembling natural waters in composition, similar results are obtained, drying at 103° in presence of excess of sodium carbonate giving numbers 0.51—2.19% in excess, whilst at 110° the divergence varies from 0.29% to 1.69%; in general, the difference between the values obtained at 103° and at 110° does not exceed 0.5%, and the use of the lower temperature is recommended, since decomposition of the organic matter and of certain of the inorganic salts present is thereby restricted.

Investigation has also been made, with solutions containing a single salt and with others resembling natural waters in composition, of the variation with the concentration of the magnitude of the coefficient  $C = M/\kappa \cdot 10^6$ , where  $M$  represents the number of milligrams of salt present per litre, and  $\kappa$  the specific conductivity in reciprocal ohms at 18°. With sodium and potassium salts and with calcium chloride,  $C$  increases gradually with the concentration, but with calcium and magnesium sulphates the increase is decidedly more rapid, so that the selection of a mean value of  $C$  is possible only within very narrow limits of concentration. Since the great majority of natural waters contain 0.2—0.3 gram of solids per litre, all waters should be diluted to this concentration with pure, distilled water before their conductivities are measured. For a number of mixed salt solutions of such concentrations and having compositions such as are met with in natural waters, the mean value of  $C$  is found to be 0.668. The formula for calculating the amount of dry residue from the conductivity then assumes the form:  $M = \kappa_x \cdot 10^6 \cdot x \cdot C$ , where  $M$  represents the residue in milligrams per litre obtained by evaporating with sodium carbonate and drying at 103°,  $x$  is the extent to which the water is diluted, and  $\kappa_x$  is the conductivity at a dilution corresponding with 0.003—0.004 gram-equivalent per litre, for which  $\kappa_{18} \cdot 10^6$  has the value 300—400 at 18°.

With natural waters of different types, the value of  $C$  varies very considerably, more particularly with the permanent hardness (magnesium and calcium sulphates) and with the chlorine; the authors recommend that, in calculating the dry residue of a water from its conductivity, the value of  $C$  taken should be as follows: For a soft water with a high chlorine-content (more than 50 mg. per litre), 0.670; for a hard water containing little chlorine (less than 20), 0.725; and for all other waters, 0.695. In all cases air should be bubbled through the water for an hour prior to the measurement of the conductivity.

Frequent measurements of the conductivity were made during the seven months, October—April, for an artesian well water and for the Moscow water-supply, which is of river origin. With the

former, the value of  $\kappa_{18} \cdot 10^6$  varied only from 602.0 to 609.3, whilst with the river water the conductivity showed a decided fall in October, as a result of heavy rainfall, and an enormous fall in March, owing to the introduction of large volumes of ice- and snow-water into the river; in this case the limiting values of  $\kappa_{18} \cdot 10^6$  were 124.5 and 450.8. It is evident that systematic measurement of the conductivity furnishes a valuable means of controlling the composition of a water-supply.

The results of preliminary experiments indicate that conductivity measurements may also serve for the estimation of the permanent and temporary hardness of a water. The hardness, in German degrees, is expressed by the following empirical formula:

$$H = H_t + H_p = (\kappa_n + \kappa_k) / A_t + y \{ (\kappa_k + \kappa_c - x_p - \kappa_0) / A_p + 1 \},$$

where  $H_t$  and  $H_p$  represent respectively the temporary and permanent hardness,  $\kappa_n$  the conductivity of the original water,  $\kappa_k$  that after boiling for an hour,  $\kappa_c$  that of a solution of sodium carbonate containing 0.01 gram-equivalent per litre,  $\kappa_0$  that of the water after treatment with sodium carbonate,  $x_p$  the corresponding correction for change of concentration,  $y$  the extent to which the water is diluted before its conductivity is measured, and  $A_t$  and  $A_p$  the magnitudes of the conductivity corresponding with 1 degree of temporary and permanent hardness respectively. The value of  $A_t$  for river water is 25, and for artesian well water, 22, whilst the value of  $A_p$  varies with  $(\kappa_k + \kappa_c - x_p)$  from 23 to 25. Application of this method to various river and well waters gives results in moderately good agreement with those obtained directly.

T. H. P.

**Hydrolytic Reactions which Take Place During the Estimation of the Total Solids in Waters.** P. KACHINSKI (*Ann. Chim. anal.*, 1913, 18, 385—389).—During the evaporation of saline solutions containing magnesium salts, hydrolysis of the latter occurs, and loss of chlorine, bromine, and iodine takes place. This loss is accentuated when the dry residue is incinerated, and, as regards the chlorides, may amount to about 50% of the total chlorine present.

W. P. S.

**Estimation of Hardness in Water by Blacher's Method.** WALTER PFLANZ (*Chem. Zentr.*, 1913, ii, 1164—1165; from *Mitt. K. Landesanst. Wasserhyg.*, 1913, 141—148. Compare this vol., ii, 153, 338).—Dimethylaminoazobenzene possesses no advantage over methyl-orange as an indicator in this method; even in the case of waters containing humic substances, methyl-orange may be used, provided that the water is titrated with  $N/10$ -acid until distinctly acid towards this indicator, and the excess of acid then titrated with  $N/10$ -alkali, using phenolphthalein as indicator. It is essential that the potassium palmitate solution employed in the process should be free from stearic acid.

W. P. S.

**Volatility of Sodium Chloride in Presence of Potassium Chloride.** M. WAGENAAR (*Pharm. Weekblad*, 1913, 50, 1214—1215).—In estimating the alkali metals in potable waters there is no

danger of altering the relative proportions of the chlorides of sodium and potassium by igniting the chloride mixture.

A. J. W.

**Estimation of the Alkali Hydrogen Carbonate Content of Natural Waters.** PIETER A. MEERBURG (*Chem. Weekblad*, 1913, 10, 958—959).—The amount of alkali hydrogen carbonate in natural waters can be estimated by evaporation of 1—3 litres to small bulk, filtration, titration of the alkali hydrogen carbonate in the filtrate with *N*/10-hydrochloric acid and methyl-orange, and estimation of the magnesium. A simpler method involves the estimation of the alkali and the determination of the hardness, but the results of the two methods do not always agree. A. J. W.

**The Estimation of Calcium Oxide Mixed with Calcium Hydroxide.** GEORG WEISSENERGER (*Österr. Chem. Zeit.*, 1913, [2], 16, 192—193).—A discussion of the errors resulting from the method of estimating calcium by means of its combined constituents, such as the amount of water evolved by calcium hydroxide or the quantity of calcium carbonate obtained from calcium oxide; this untrustworthiness is demonstrated by the analysis of mixtures containing known proportions of calcium oxide and hydroxide. F. M. G. M.

**Estimation of Calcium as Oxalate.** SAMUEL GOY (*Chem. Zeit.*, 1913, 37, 1337—1338).—Calcium may be conveniently estimated as hydrated calcium oxalate, but in order to obtain correct results the following conditions should be observed.

The calcium should be precipitated by ammonium oxalate at the boiling heat, and the oxalate collected in a Gooch crucible in connexion with a suction apparatus. After washing the precipitate with small quantities of water until free from ammonium oxalate, the crucible and contents are dried for four to five hours at exactly 105°. The dried compound has the composition  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . Drying on a filter gives erroneous results.

L. DE K.

**Detection of the Metals of the Alkaline Earths by Spectrum Analysis in the Course of Qualitative Analysis. II.** ERNST H. RIESENFELD and G. PFÜTZER (*Ber.*, 1913, 46, 3140—3144. Compare A., 1906, ii, 804).—An apparatus for the production of an arc spectrum between an iridium electrode and a small quantity of a solution is described. The liquid is contained in a 1—2 c.c. glass tube, through the bottom of which a platinum lead is fused. The electrode may be raised or lowered over the liquid by means of a micrometer screw, and other screws facilitate the adjustment of the whole device before the slit of a spectroscope. The chief magnesium lines may be detected in the arc spectrum in a dilution of 0.1 mg. per c.c., the calcium lines with 0.002 mg. per c.c.; strontium, 0.03 mg. per c.c.; and barium, 0.006 mg. per c.c. Large excesses of the other earths are no drawback to the detection of magnesium. The arc spectra are 20 to 2000 times as sensitive as the flame spectra.



The procedure is not advantageous in the case of potassium, but the sodium line,  $568\cdot6\mu\mu$ , appears with  $0\cdot04$  mg. of the metal per c.c., and may thus be taken as an indication of the presence of weighable quantities in a solution. J. C. W.

#### Radio-elements as Indicators in Analytical Chemistry.

FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1915, 34, 1401—1407).—The chemical non-separability of lead and radio-lead, or radium-*D*, lends itself to the use of radium-*D* as an indicator for lead in quantities too small to be otherwise estimated. The quantities necessary for detection are  $10^{-10}$  gram of radium-*D* by the  $\beta$ -rays of radium-*E*, and  $10^{-12}$  gram by the  $\alpha$ -rays of radium-*F* by waiting until the latter attains equilibrium (a year or more). The radio-lead from pitchblende contains about  $10^{-7}$  gram of radium-*D* per gram, so that about 1 mg. can be detected by the  $\beta$ -ray method. For more sensitive measurements the radium-*D* content must be increased by addition of the products of radium emanation. The products of 0·2 curie were mixed with 10 mg. of lead chloride, potassium chromate was added, and the liquid made up to 100 c.c. was shaken in a thermostat at  $25^\circ$  for twenty-four hours. The activity of the evaporated filtrate was measured after radium-*E* had reached equilibrium by comparing it with that of 1 c.c. of the original solution before precipitation, and corresponded with that of 0·012 mg. of lead chromate per litre. Lead chromate is the least soluble lead salt, the solubility of lead phosphate being of the same order. Similarly the solubility of lead sulphide was found to be in pure water at  $25^\circ$  0·3 mg. per litre, and in water saturated with hydrogen sulphide 0·15. Similarly, radium-*E* may be used as an indicator for bismuth, and ionium as an indicator for thorium. F. S.

#### Cathodic Estimation of Lead and Analysis of Lead Alloys.

R. GARTENMEISTER (*Chem. Zeit.*, 1913, 37, 1281—1282).—The author finds that gallic acid is a suitable addition-agent, in the electrolysis of solutions of lead salts, for preventing the deposition of lead dioxide at the anode and the evolution of hydrogen at the cathode. Quantitative deposits of lead on the cathode may be obtained by observing the following conditions. For estimating quantities of lead up to 1 gram, the electrolyte should have a volume of about 125 c.c., and contain 2—2·5 c.c. of nitric acid (D 1·4), 5 grams of gallic acid, and 5—6 c.c. of alcohol. The anode should be a cylinder of platinum foil and be surrounded by a Winkler cylindrical gauze cathode. Using a current of 1·2 amperes, the time of electrolysis (stationary electrodes) is four hours at  $65$ — $70^\circ$  for 1 gram of lead. This time must not be exceeded to any great extent, otherwise a yellow dye is deposited.

Zinc, cadmium, iron, nickel, cobalt, and manganese are not deposited under the above conditions. Silver, tin, arsenic, and antimony form black, rough deposits. Bismuth is precipitated as bismuth gallate, and does not interfere. Copper is deposited with the lead.

Alloys of lead, tin, and antimony are best analysed as follows. One to two grams of the alloy are dissolved in a mixture of nitric and tartaric or citric acids. The solution is made alkaline with sodium hydroxide, and then precipitated with sodium sulphide. The lead sulphide is collected, washed with sodium sulphide solution, and finally with a strong solution of ammonium chloride containing some ammonium hydroxide and ammonium sulphide. The lead sulphide, which may also contain copper, iron, and zinc sulphides, is dissolved in nitric acid, the solution filtered, the filter paper ashed, and the ash dissolved in nitric acid and added to the solution, which is then evaporated to dryness. The residue is taken up with nitric acid, and the lead estimated as above. The weight of the deposit has to be corrected for copper, which is estimated separately. The antimony and tin in the filtrate from the lead sulphide are estimated electrolytically in the usual way. T. S. P.

**Detection of Lead in Bismuth Subnitrate and Bismuth Carbonate.** GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1913, [vii], 8, 422—424).—The test depends on the insolubility of bismuth subnitrate in ammonium nitrate solution, whilst lead sulphate, carbonate, etc., are soluble. Further, bismuth carbonate is converted into bismuth subnitrate when boiled with ammonium nitrate solution. For the detection of lead in bismuth subnitrate, 10 grams of the sample are boiled for three minutes with 50 c.c. of 5% ammonium nitrate solution; the mixture is then cooled, filtered, and the filtrate is tested with potassium chromate solution; the test will detect the presence of 1 mg. of lead in 10 grams of the subnitrate. In the case of bismuth carbonate, 10 grams are heated to boiling with 100 c.c. of 5% ammonium nitrate solution, the mixture is evaporated to dryness, 100 c.c. of water are added to the residue, and evaporated to a volume of about 40 c.c. It is essential to expel completely the ammonium carbonate resulting from the reaction. When cold, the mixture is filtered, and the filtrate tested as described. W. P. S.

**Estimation and Detection of Lead in Organic Materials and the Separation of Lead and Calcium Sulphates by Ammonium Acetate.** ERNST ERLÉNMYER (*Biochem. Zeitsch.*, 1913, 56, 330—340).—The organic material is incinerated, and the ash is digested with 20% sodium carbonate. The insoluble residue is then digested with 5*N*-nitric acid, and the greater part of the lead is dissolved. The insoluble residue still contains lead, and is fused with sodium and potassium carbonate mixture. The fusion is then extracted with 5% sodium carbonate, the insoluble residue containing the lead is extracted with nitric acid, and this extract is added to the nitric acid solution containing the main bulk of the lead. The solution of lead in nitric acid is evaporated on a water-bath, the residue is extracted with water, ammonia is added until alkaline reaction, then acetic acid until acid reaction, and the mixture is then digested for two hours. The aluminium and iron and the greater part of the calcium remain undissolved, and in the filtrate from these the lead is precipitated by the addition of ammonium

dichromate added as powder. The lead chromate is then converted into the sulphate and weighed as such. For qualitative analysis the ash is extracted with nitric acid, the lead is precipitated as sulphate by addition of sulphuric acid and concentration, and the precipitate, after washing with 4% sulphuric acid, is treated with hydrogen sulphide, the formation of the black sulphide indicating the presence of lead. Lead and calcium sulphates can be separated by treating them with a mixture of equal volumes of alcohol and concentrated ammonium acetate, in which the lead sulphate is much more readily soluble.

S. B. S.

[Estimation of Copper. Iodometric Estimation of Iron.]  
CHR. BECK (*Chem. Zeit.*, 1913, **37**, 1330—1331).—*Estimation of Copper as Cuprous Sulphide*.—The usual method (ignition of copper sulphide + sulphur in a Rose's crucible) is employed, with this difference, however, that instead of a current of hydrogen or hydrogen sulphide, a current of carbon dioxide is used. The crucible should be heated over a full Bunsen flame.

*Iodometric Estimation of Iron*.—The iron which should be present in the ferric state is distilled in a suitable apparatus with dilute hydrochloric acid (1:2) and about 2 grams of potassium iodide, with addition of a few lumps of marble to generate an atmosphere of carbon dioxide. The iodine liberated is distilled off and collected in a suitable receiver containing 2 grams of potassium iodide dissolved in 100 c.c. of water; the receiver should be cooled by ice-water. When the bulk of the liquid has passed over, the receiver is at once disconnected (before turning off the gas) and the contents titrated with sodium thiosulphate.

L. DE K.

*Analysis of Alloys Containing Copper, Nickel, and Zinc [German Silver, Alpaka, etc.]*. CHARLES LIND (*Chem. Zeit.*, 1913, **37**, 1372).—The alloy (0.5 gram) is dissolved in concentrated nitric acid (10 c.c.). The solution is boiled, diluted with water (50 c.c.), and rendered alkaline by addition of concentrated ammonia solution. Excess of ammonia is removed by nitric acid (D 1.18), a further 3 c.c. of this acid are added, the solution diluted to 100 c.c., heated to boiling, and the copper determined electrolytically. Deposition is complete in fifty minutes when rotating platinum gauze electrodes are used, the current being 3 amperes and potential difference 3 volts.

For the estimation of zinc, the residual solution is neutralised with ammonia, acidified by two drops of nitric acid (D 1.18), heated to about 50°, and treated with hydrogen sulphide for an hour. The precipitated zinc sulphide is collected, washed with a solution of ammonium chloride (2 grams in 100 grams of water), and dissolved in dilute sulphuric acid. After treatment with potassium hydroxide (10 grams), the solution is diluted to 100 c.c., and the zinc deposited electrolytically on the coppered platinum gauze electrodes (obtained above). The current employed is 0.8—1 ampere, the potential difference 4 volts. With rotating electrodes, 0.1 gram of zinc is quantitatively deposited in sixty minutes.

Nickel is determined in the filtrate from the zinc sulphide by the dimethylglyoxime method.

The process is accurate, and can be carried out in a comparatively short time. It has the further advantage that small quantities of impurities, such as tin, lead, iron, and manganese, can be simultaneously estimated.

H. W.

**Estimation of Free Acid and Basicity of Aluminium Sulphate.** W. N. IVANOV (*Chem. Zeit.*, 1913, **37**, 805—806).—The methods of estimating free acid, or, in its absence, the basicity of aluminium sulphate, may be divided into three groups depending on: (1) direct titration with various indicators; (2) precipitation of aluminium hydroxide by magnesium ammonium phosphate and titration of the acid in the filtrate; and (3) Beilstein and Grosset's method (A., 1890, 85), in which the substance is dissolved in water, treated with saturated ammonium sulphate solution, and finally with alcohol. The precipitate is filtered and washed with alcohol, the alcoholic filtrate being evaporated, the residue dissolved in water, and titrated with  $N/2$ -sodium hydroxide in the presence of methyl-orange. The first two methods gave unsatisfactory results. The third method is also found to be untrustworthy, since the amount of free acid found depends on the quantity of water and alcohol used, and can amount to the sum of free and combined acid actually present. Under the usual analytical conditions, a content of 0.25% free acid can easily be found in a preparation which actually has a 90% basicity.

H. W.

**Electrolytic Reduction of Iron for Analysis.** J. CLYDE HOSTETTER (*J. Washington Acad. Sci.*, 1913, **3**, 429—432).—The following method is proposed for the reduction of ferric sulphate for subsequent titration with permanganate. The ferric sulphate solution, measuring about 300 c.c., is placed in a gold basin, and 10 c.c. of sulphuric acid, D 1.84, are added; a porous cell is now placed in the solution, and filled with dilute sulphuric acid (1 : 30). A piece of platinum foil (area 28 sq. cm.) is inserted in the porous cell, and serves as the anode, whilst the gold basin acts as the cathode. A current of about 8 amperes is passed through the solution for seventy minutes (0.5 gram of iron is reduced to the ferrous condition in this time), the contents of the anode chamber are then transferred to the basin, the chamber is refilled with dilute acid, and the electrolysis is continued for a further ten minutes. The solution in the basin is then titrated with permanganate solution. Before the titration, a drop of the solution may be tested with thiocyanate to ascertain whether the reduction has been completed.

W. P. S.

**Analysis of Commercial Nickel.** L. BERTIAUX (*Ann. Chim. anal.*, 1913, **18**, 377—385).—Methods are given for the estimation of such impurities as copper, cobalt, iron, manganese, aluminium, calcium, magnesium, sulphur, silicon, carbon, arsenic, and antimony in commercial nickel. The following is an outline of the procedure

recommended. The metal is dissolved in a mixture of hydrochloric and sulphuric acids, the solution is rendered ammoniacal, and the nickel, cobalt, and copper are deposited electrolytically. The deposit consisting of the three metals is then dissolved in nitric acid, the copper is deposited from this solution, the cobalt is precipitated as potassium cobaltinitrite, and the nickel remaining in solution is estimated electrolytically. Iron, manganese, aluminium, calcium, and magnesium are estimated in the solution after the removal of the nickel, cobalt, and copper. Silica and sulphur are estimated in a separate portion of the sample in the usual way. The distillation method is employed for the estimation of the arsenic and antimony, and the carbon is estimated by combustion.

W. P. S.

**Titration of Titanium by means of Methylene-blue.** BERNHARD NEUMANN and ROBERT K. MURPHY (*Zeitsch. angew. Chem.* 1913, 26, 613—616).—The authors have investigated and confirm the accuracy of Knecht and Hibbert's method of titrating titanium with methylene-blue (compare Knecht, A., 1907, ii, 654; Hibbert, A., 1909, ii, 351). The reaction proceeds according to the equation:  $C_{16}H_{18}N_3ClS + 2TiCl_3 + HCl = C_{16}H_{18}N_3S + 2TiCl_4$ , and is exactly molecular, but, owing to the difficulty of obtaining the pure dye, the solution employed must be standardised. Best results are obtained with 0.02—0.04*N*-solutions, made by dissolving 3.9 to 7.8 grams of the dye in hydrochloric acid and filtering into dark glass bottles. The controlling solution is made from Merck's 15% solution of titanous chloride, in which case titanium is first separated from the accompanying ferrous chloride and estimated by gravimetric methods, or pure titanic oxide may be prepared from titanic acid, which usually contains silica and oxides of iron and aluminium, by the method of Bornemann and Schirmeister (A., 1910, ii, 1073). The strongly acid solution of titanium chloride is then reduced by zinc dust and filtered into a flask, which is fitted with an inlet tube and a Bunsen valve. To complete the reduction, a clean zinc rod is suspended in the liquid, and this is kept nearly boiling, whilst a stream of carbon dioxide is admitted. The zinc rod is then removed, the burette is inserted into the valve, and the methylene-blue solution is run in until the blue colour is permanent. The bulk of the liquid should be about 150 c.c. (compare Hibbert, *loc. cit.*).

For the estimation of titanium, the substance is fused with sodium hydroxide and sodium peroxide, and then dissolved in concentrated hydrochloric acid. If sulphuric or nitric acid is used to dissolve the sample, the titanium must be precipitated by ammonia and re-dissolved in hydrochloric acid. The reduction and titration are then carried out as above, the process requiring about forty-five minutes after the fusion. Iron, even in overwhelming proportion, aluminium, silicon, calcium, alkalis, magnesium, zinc, antimony, arsenic, and phosphorus do not influence the titration, but salts of the lower oxides of tin, vanadium, or tungsten, and also sulphurous acid, must not be present.

The method is useful when mere traces of titanium are present, is more accurate than the known methods (a critical review of which is given), and is the only one which permits of the direct estimation of titanium in presence of iron, silica, or alumina. J. C. W.

**Assay of Platinum Ores.** MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, **52**, 740—752).—The process is practically the old one of Saint-Claire Deville and Debray incorporated with the authors' new processes for the estimation of palladium. L. DE K.

**Estimation of Palladium with Nitroso- $\beta$ -naphthol in Presence of Copper and Iron.** MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, **52**, 737—739).—The solution containing about 0.25 gram of palladium and small quantities of copper and ferric iron, all present as chlorides, is diluted to about 150 c.c., 20 c.c. of strong hydrochloric and 20 c.c. of glacial acetic acid are added, and then, after heating to boiling, a hot solution of nitroso- $\beta$ -naphthol in 50% acetic acid is added in excess. On prolonged boiling, a voluminous Kermes-coloured precipitate collects on the surface, which is at once collected on a filter and washed, first with hot 5% hydrochloric acid, and then with hot water. It is then converted into metallic palladium by igniting the filter and contents, first in the air and then in a current of hydrogen; the metal is allowed to cool in a current of carbon dioxide.

The filtrate is nearly neutralised with ammonia, and the copper precipitated as cuprous thiocyanate in presence of sulphurous acid, and weighed as such. The filtrate, after boiling with a little nitric acid, is treated for iron as usual. L. DE K.

**Observations of the Abel Heat Test.** B. JAMES SMART (*J. Soc. Chem. Ind.*, 1913, **32**, 967).—The author discusses and criticises a recent paper by Egerton (this vol., ii, 534). W. P. S.

**The Tailameter: A Simple Apparatus for the Rapid Estimation of Volatile Oils in Aromatic Plants, Drugs, and Spices.** PROBODHA C. CHATTOPADHYAY (*J. Soc. Chem. Ind.*, 1913, **32**, 968).—The apparatus consists of a 500 c.c. flask, the neck of which is graduated into 10 c.c. in one-tenth divisions; a "swan-neck," provided with a tap, is fused into the lower portion of the flask. The distillate obtained on steam-distilling a material containing volatile oils is collected in this flask, and at the end of the distillation, the oil on the surface of the water is brought into the graduated portion of the neck by the addition of more water, and its volume is ascertained. W. P. S.

**Simultaneous Estimation of Methyl Alcohol and Formaldehyde in Small Quantities in the Same Solution.** MAURICE NICLOUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 935—939).—The author has described previously (A., 1899, ii, 253) methods for the estimation of methyl alcohol and formaldehyde separately. The method now described is suitable for both substances in the same

solution, and depends on (1) the estimation of the quantity of potassium dichromate required for complete oxidation of both substances; and (2) the determination of the amount of carbon dioxide produced in the reaction. Exact details of the methods of working and of the calculations required are given. T. A. H.

**Estimation of Small Quantities of Methyl and Ethyl Alcohols in Aqueous Solutions of the Same.** JÓSEF HETPER (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 342—348).—The method proposed depends on the oxidation of the alcohols by permanganate in acid and in alkaline solution, and is applicable to solutions containing from 0·1 to 0·25% by weight of the two alcohols. Formulæ are given for calculating the quantities of the two alcohols present from the amount of permanganate consumed in the two oxidations (see also this vol., ii, 158). W. P. S.

**Methods for Testing Ether.** GEORG FRERICHS (*Chem. Zentr.*, 1913, ii, 1254—1255; from *Apoth. Zeit.*, 1913, **28**, 628—630).—Ether which has been prepared from alcohol denatured with wood-spirit and pyridine will contain methyl ethyl ether and acetone; the pyridine remains in the sulphuric acid. Pure ethyl ether has b. p. 34·2—34·3°/1760 mm.; this constant is affected by the presence of methyl ethyl ether, and is raised by 0·2° for each 1% of alcohol which may be present. The boiling point of ether should be determined under a reflux, and a piece of apparatus for this purpose is described. Acetone may be detected in ether by shaking 100 c.c. of the sample with 10 c.c. of water, separating the aqueous layer, and submitting portions of it to the iodoform and sodium nitroprusside tests. W. P. S.

**Testing Amyl Acetate.** A. HÄMMELMANN (*Chem. Zentr.*, 1913, ii, 1335; from *Farbenzeit.*, 1913, **18**, 2594—2595).—Wolff's method of testing amyl alcohol or amyl acetate for the presence of benzene, based on the solubility of the sample in sulphuric acid, D 1·80, is untrustworthy, since pure amyl alcohol or acetate may yield insoluble alkylene compounds under the conditions of the test. W. P. S.

**Testing Amyl Acetate.** H. WOLFF and B. ROSUMOFF (*Chem. Zentr.*, 1913, ii, 1335; from *Farbenzeit.*, 1913, **18**, 2641—2642).—Hämmelmann's objection to Wolff's test (see preceding abstract) may be overcome by carrying out the test as follows. The amyl acetate is mixed slowly with 1·5 times its volume of sulphuric acid, D 1·80, the mixture being kept cold and not shaken violently during the operation. When less than 5% of benzene is present, the mixture remains quite clear. W. P. S.

**Ignition of Sugar Syrup.** M. WAGENAAR (*Pharm. Werkblad*, 1913, **50**, 1213—1214).—In estimating calcium and phosphates in sugar syrup, the sample can be readily ignited to a white ash by transferring it drop by drop to a red-hot platinum dish, the beaker

employed being subsequently weighed to ascertain the weight of syrup taken.  
A. J. W.

**Estimation of the Sugar in Blood.** WALTER GRIESBACH and H. STRASSNER (*Zeitsch. physiol. Chem.*, 1913, 88, 199—209).—The blood is first deprived of proteins, preferably by colloidal iron. Estimations of the sugar in the filtrate by the polarimeter and by reduction give the same values for dextrose. After fermentation with yeast, the filtrate exhibits neither reduction nor optical activity. Of the reduction methods used, that of Maquenne and of Bertrand yield almost identical results. Other methods (Bang's, Tachau's, etc.) were also employed. Maquenne's method is recommended on account of its certainty and simplicity. Briefly, it consists in boiling with Fehling's solution, followed after cooling by the addition of potassium iodide and sulphuric acid. Starch is then added, and the free iodine titrated back with thiosulphate.

W. D. H.

**Estimation of Hydroxy-fatty Acids in Fat by means of Organic Magnesium Compounds.** TH. ZEREVITINOV (*Zeitsch. anal. Chem.*, 1913, 52, 729—737).—The total fatty acids are isolated in the usual manner, and carefully dried. About 0.2 gram of the acids is dissolved in pyridine, and to this is then added in a suitable apparatus a solution of magnesium methyl iodide in amyl ether. The gas evolved (methane) is then measured with the usual precautions. 1 mol of methane=1 mol. of hydroxyl.

If from the result is deducted the carboxyl-hydroxyl, as found by titration with standard alkali in alcohol-ether solution, the difference will be, as the author calls it, the alcohol-hydroxyl number, which represents hydroxy-fatty acid. A large number of results relating to fatty acids and to oils are communicated.

L. DE K.

**Detection of Citric Acid in Wine, with Reference to a Recent Paper by Fresenius and Grünhut.** GEORGES DENIGÈS (*Ann. Chim. anal.*, 1913, 18, 393—402. Compare this vol., ii, 255).—The author criticises the statements of Fresenius and Grünhut (*loc. cit.*), maintains the trustworthiness of his method for the detection of citric acid, and shows that it is more sensitive than Möslinger's test. Attention is directed to the experience of other workers with Denigès' method (compare A., 1908, ii, 544, 640, 904).

W. P. S.

**Qualitative Detection of Benzoic Acid and Salicylic Acid in Milk and Beer.** M. WAGENAAR (*Pharm. Weekblad*, 1913, 50, 1215).—For the estimation of benzoic acid and salicylic acid in milk and beer, the author recommends steam distillation for several hours, neutralisation of the distillate with sodium carbonate, evaporation to small bulk, and the application of the ordinary tests for the acids named.

A. J. W.



**Microchemical Detection of Embelic Acid.** GEORG HEYL and P. KNEIP (*Chem. Zentr.*, 1913, ii, 1342; from *Apoth. Zeit.*, 1913, 28, 699).—Embelic acid, the active constituent (anthelmintic) of the fruit of the Indian shrub *Embelia ribes*, may be isolated and identified by the micro-sublimation method described by Tunmann. The crystalline sublimate obtained is insoluble in water, but dissolves in dilute sodium hydroxide, yielding a reddish-violet coloured solution; with concentrated sodium hydroxide solution, violet, crystalline plates separate out after a time, violet needles forming subsequently. These crystals yield a flocculent precipitate of embelic acid when treated with hydrochloric acid. Ammonia also dissolves the sublimate, and on evaporating the solution crystals are obtained. The dilute alkaline solution of the sublimate gives the following reactions: with copper sulphate, an olive-brown precipitate; with barium chloride, a greyish-brown precipitate; with nickel sulphate or cobalt nitrate, a greenish-brown precipitate; with magnesium sulphate, a flocculent, brown precipitate. The colour of the precipitate obtained on treating an alcoholic solution with ferric chloride is reddish-brown; with copper nitrate, dirty green; lead acetate, dark green; and with zinc chloride, violet. Mercuric chloride and silver nitrate yield no precipitate. Whilst pure embelic acid yields a violet coloration when warmed with concentrated sulphuric acid, the sublimate gives but a faint reaction when treated similarly.

W. P. S.

**The "Chlorine Number," a New Constant of Fats.** AS. ZLATAROV (*Zeitsch. Nahr. Genussm.*, 1913, 26, 348—349).—A preliminary notice of a method in which it is proposed to estimate the quantity of chlorine fixed by a fat or oil. The fat is treated with saturated solution of phenyliododichloride in carbon tetrachloride, and, after four hours' contact, the excess of the chloride is titrated with silver nitrate solution.

W. P. S.

**Modified Meig's Method for the Estimation of Fat in Milk.** WALTER LEWIS CROLL (*Biochem. Bull.*, 1913, 2, 509—518).—Meig's method is an ether-extraction method. The present paper describes certain proposed modifications which simplify and shorten it, without loss of accuracy.

W. D. H.

**Detection and Estimation<sup>3</sup> of Minute Quantities of Formaldehyde in the Presence of Hexamethyleneamine, and Methyl Alcohol in the Presence of Ethyl Alcohol.** H. A. B. DUNNING (*Amer. J. Pharm.*, 1913, 85, 453—457).—The following test may be used to detect the presence of formaldehyde in the urine of persons who have been given doses of hexamethylenetetramine. About 2 c.c. of the urine are warmed in a test-tube, 2 drops of a 0.5% phenylhydrazine hydrochloride solution are added, followed by 2 drops of a 0.5% sodium nitroprusside solution, and the mixture is then rendered strongly alkaline with sodium hydroxide. One part of formaldehyde in 50,000 parts yields a blue coloration; in more dilute solutions, a green coloration is obtained. Another test

consists in heating the urine with phloroglucinol and then adding sodium hydroxide; when a red coloration develops, formaldehyde is present. The formaldehyde may be estimated colorimetrically by treating 5 c.c. of the urine with 0.1 c.c. of a 15% sodium hydroxide solution, adding 0.1 c.c. of phenylhydrazine (base) and 0.7 gram of sodium hydroxide, and shaking the mixture for ten minutes. The coloration obtained is compared with that produced by similarly treating known quantities of formaldehyde; the comparisons must be made within twenty minutes after the addition of the sodium hydroxide. Dextrose, acetone, and acetaldehyde do not interfere with the estimation.

The method proposed for the detection of methyl alcohol in the presence of ethyl alcohol consists in saturating the mixture of the alcohols with potassium citrate (to remove the greater part of the water), and submitting the mixture to fractional distillation. The low boiling portion of the distillate is then heated in a test-tube, and a hot copper spiral is plunged in the vapour; the characteristic odour of formaldehyde will be noticed if methyl alcohol is present.

W. P. S.

**Estimation of Paracetaldehyde in Paraldehyde.** GEORG HEVL (*Chem. Zentr.*, 1913, ii, 1520; from *Apoth. Zeit.*, 1913, 28, 720—721. Compare A., 1912, ii, 304).—The method depends on the oxidation of the acetaldehyde to acetic acid by means of hydrogen peroxide in alkaline solution; the excess of the alkali is then titrated. Twenty-five grams of the paracetaldehyde are dissolved in 300 c.c. of cold water, 30 c.c. of *N*/1-potassium hydroxide solution are added, followed by 20 c.c. of 30% hydrogen peroxide solution; the mixture is kept in a closed vessel, and, after eighteen hours, the excess of alkali is titrated, using phenolphthalein as indicator. Each c.c. of *N*/1-alkali solution is equivalent to 0.04403 gram of acetaldehyde.

W. P. S.

**Detection of Hexamethylenetetramine in Wine and Milk.** LEOPOLD ROSENTHALER and E. UNGERER (*Pharm. Zentr.-h.*, 1913, 54, 1153—1155).—Mercuric chloride is the most sensitive reagent for the detection of hexamethylenetetramine; 1 part of the latter in 500,000 parts of solution yields a characteristic crystalline precipitate with the reagent. White wine may be tested directly after the addition of a small quantity of hydrochloric acid, but in the case of red wine it is necessary to treat the sample with solid lead acetate and remove the excess of lead with sodium phosphate before the test is applied. In testing milk, a portion of the sample is treated with hydrochloric acid, saturated with ammonium sulphate, filtered, and the filtrate used for the test. The mercuric chloride precipitate may be further tested by applying to it the morphine-sulphuric acid test, or it may be distilled from a sulphuric acid solution, and the resulting formaldehyde identified.

W. P. S.

**The Gasometric Estimation of Aliphatic Amino-nitrogen in Minute Quantities.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, 16, 121—124).—By a modification (mainly reduction of size) of

the apparatus previously described (A., 1912, ii, 1008), the author's method is brought within the class of micro-methods, and remains accurate.

W. D. H.

**Improved Methods in the Gasometric Estimation of Free and Conjugated Amino-acid Nitrogen in the Urine.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, 16, 125—134).—The author's previously published process (A., 1912, ii, 1008) for estimating total (free and conjugated as hippuric acid, peptides, etc.) amino-acid nitrogen can be simplified, so that the operations are shortened, and the more laborious parts, such as boiling off ammonia and washing milky precipitates, are dispensed with. The free amino-acids alone can readily be estimated after decomposition of the urea with soy-bean urease, which hydrolyses urea completely without either freeing conjugated amino-acids or deaminising free ones. The applicability of the gasometric method for the estimation of hippuric acid is also indicated.

W. D. H.

**The Separation of *d*-Alanine and *d*-Valine.** PHŒBUS A. LEVENE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, 16, 103—120).—*d*-Alanine combines with phosphotungstic acid in the approximate ratio 1:14 by weight, forming a crystalline salt. At 0° in a solution containing per 100 c.c. 20 grams or more of phosphotungstic acid (in excess of the amount combining with the alanine) and 10 grams of sulphuric acid, the solubility of alanine is only 0.15 gram. The solubility of *d*-valine under the same conditions is 1.21 grams per 100 c.c. By alternate crystallisation of valine as the free amino-acid and of alanine as the phosphotungstate, a practically quantitative separation of the two acids in admixture can be effected.

W. D. H.

**Estimation of Urea [Carbamide].** H. T. B. RASMUSSEN (*Chem. Zentr.*, 1913, ii, 1335; from *Skand. Arch. Physiol.*, 1913, 30, 191—195).—The methods proposed by Christensen (*Nord. med. arkiv.*, 1886, 18), and by Henriques and Gammeltoft (A., 1911, ii, 670) were investigated. The former, depending on the hydrolysis of the urea by heating with water under pressure and estimating the resulting carbon dioxide, yields trustworthy results in the case of urea itself, but the results are too high when the method is applied to urine. Henriques and Gammeltoft's method gives lower, and apparently more trustworthy, results.

W. P. S.

**Estimation of Nicotine in the Form of Silicotungstate.** ROSARIO SPALLINO (*Gazzetta*, 1913, 43, ii, 482—486).—This method gives good results if the product is calcined and weighed in the form of the residue  $WO_3 + SiO_2$  so obtained, but not if the silicotungstate is weighed after mere drying at 125°, as has been recommended recently.

*Nicotine dipicolonate*,  $2C_{10}H_8O_5N_4 \cdot C_{10}H_{14}N_2$ , forms canary-yellow crystals, m. p. 223°.

R. V. S.

**New Method of Estimating Nicotine in the Presence of Ammonia.** ROSARIO SPALINO (*Gazzetta*, 1913, 43, ii, 493—500).—The methods which have been proposed for this purpose do not yield concordant results. The present method depends on the fact that nicotine behaves as a diacidic base towards picric acid in aqueous solution, but in alcoholic solution it behaves as a monoacidic base. The liquid containing nicotine is treated with an excess of picric acid solution of known strength (0.009 mg. per c.c.). The liquid so obtained is made up to 1 litre with alcohol, and divided into two equal portions, which are then evaporated to dryness. In one case the residue is dissolved in alcohol, and titrated with *N*/20-barium hydroxide. The other is treated with water, made up to 100 c.c., and filtered to remove precipitated picrate; of this solution 75 c.c. are titrated with barium hydroxide as before. No ammonia is lost in the evaporation. The difference between the two titrations (regard being had to the 25 c.c. of aqueous solution not titrated) gives the amount of picric acid present. The method gives accurate results with the solutions of picric acid of known strength in the presence of ammonia, and yields concordant figures in duplicate analyses of ammoniacal distillates from tobacco.

R. V. S.

**The Triketohydrindene Reaction.** CARL NEUBERG (*Biochem. Zeitsch.*, 1913, 56, 500—506).—A distillate from hexanol gave a positive reaction, and on investigation it was found that substances other than amino-acids gave a positive reaction, which could be distinguished from that given by sugars in alkaline solution recently described by Halle, Loewenstein, and Pfibram (this vol., ii, 992). These substances included: I. Amines, which give a direct positive reaction when in combination with weak alkalis. II. Amino-aldehydes, which give a positive reaction when free, or a salt of weak acids. III. Urea derivatives like allantoin, which give the reaction with a pink tinge. IV. Aminosulphonic acids, such as taurine. V. Ammonium salts of aldehyde and keto-acids. VI. Certain organic acids, dicarbonyl compounds, and halogen aldehydes, which have been treated with ammonia in excess, and then freed from this reagent by boiling. The following acids illustrate this reaction: glycollic, lactic, glyceric, malic, and citric acids. Bromal hydrate, phenylglyoxal, and alloxan also give the reaction. The following substances gave a negative or abnormal (colour) reaction: indole, quinoline, isoquinoline, cinchonine, brucine, quinidine, morphine, allylthiocarbimide (red), allylamine (yellowish-red), diethylamine (red), piperidine, cyanoacetic acid, thiosinamine, lecithin, betaine, potassium ferrocyanide, choline, camphylamine (red), formamide, amygdalin, diacetoneamine, adenine, xanthine, creatine, creatinine, ethyl  $\beta$ -aminocrotonate, trimethylsulphine iodide, aniline, chondroitinsulphuric acid, aminosulphonic acid, barbituric acid, hydrazine, and phenylhydrazine.

S. B. S.

**Precipitation by Zinc Salts of the Purine Bases from Urine and Meat Extracts.** H. THAR (*Biochem. Zeitsch.*, 1913, 56, 353—354).—Reply to E. Salkowski (this vol., ii, 992). S. B. S.

**Urobilin and its Detection by Treating Urine with Copper Sulphate and Extraction with Chloroform.** THEODOR HAUSMANN (*Chem. Zentr.*, 1913, ii, 819; from *Zeitsch. exper. Path. Ther.*, 1913, 13, 373—399).—The method depends on the fact that the urobilinogen of urine is oxidised by copper sulphate to urobilin, which may be extracted with chloroform. Twenty c.c. of the urine are mixed with 2 c.c. of 10% copper sulphate solution, and the mixture is shaken with 2 c.c. of chloroform; the chloroform layer is coloured pink, orange, or red. In the case of very acid urines the colour obtained is yellow. If, in place of copper sulphate, the urine is treated with a concentrated solution of either ferrous sulphate, zinc acetate, zinc sulphate, or potassium ferricyanide, the chloroform layer remains colourless, whilst lead acetate, mercuric chloride, and phosphotungstic acid yield precipitates with the urine, and only a small proportion of the urobilin is extracted by the chloroform; repeated extractions are necessary to obtain all the urobilin in the chloroform solution. Previous treatment of the urine with formaldehyde or dimethylaminobenzaldehyde hinders the oxidation of the urobilinogen by copper sulphate. The chloroform extract contains the actual urobilin and not its copper compound; the urobilin may be extracted from the chloroform solution by shaking the latter with sodium hydroxide solution. This alkaline solution exhibits the characteristic properties of a urobilin solution (absorption bands, fluorescence with alcoholic zinc acetate, etc.). For the estimation of the urobilin, the chloroform extract is evaporated to dryness, the residue is dissolved in  $N/10$ -sodium hydroxide solution, and the excess of the latter is titrated with  $N/10$ -hydrochloric acid; the difference between the quantities of alkali and acid solutions used is multiplied by 0.0062 to give urobilin.

W. P. S.

**Detection of Indoxyl in Icteric Urine.** LOUIS BÉLIÈRES (*J. Pharm. Chim.*, 1913, [vii], 8, 429—430).—The presence of biliary pigments in the urine is ascertained by a preliminary test in which the urine is treated with an excess of basic lead acetate, the precipitate collected on a filter, washed with water, and then transferred to a test-tube, in which it is mixed with 20 c.c. of 9% alcohol. Hydrochloric acid is then added; the lead chloride settles rapidly, and the alcohol exhibits a green colour. The development of the coloration may be accelerated by the addition of a few drops of hydrogen peroxide solution. For the detection of indoxyl, the urine is treated with basic lead acetate, and filtered. A portion of the filtrate is mixed with an equal volume of hydrochloric acid, and shaken with chloroform; the latter exhibits the characteristic coloration. Another portion of the filtrate is treated with ammonia, the precipitate is collected on a filter, and treated with alcohol and an excess of hydrochloric acid; the alcoholic solution is coloured reddish-violet. After filtration, the solution is diluted with water and shaken with chloroform, when the latter is coloured blue, red, or violet.

W. P. S.

**Substances in Urine giving Rise to Indigotin. II. New Qualitative Tests.** ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, 88, 47—55. Compare this vol., i, 1134).—Most of the existing methods for the detection of indigotin-forming substances in urine differ only in the use of different oxidising agents, and they are all untrustworthy. The decolorisation of the indigotin solutions frequently observed is due to the presence of oxidising chloro-compounds in the chloroform used. These can be removed without difficulty, and the conditions are given for carrying out the test in the absence of air, when pure blue solutions are obtained, which can be compared colorimetrically with Fehling's solution. An alternative method is to add isatin and hydrogen chloride, and convert the indigotin compound into indirubin. When air is excluded in this case also, the method becomes more delicate, and can be applied to quantitative measurements. E. F. A.

**Nephelometric Determination of Proteins: Casein, Globulin, and Albumin in Milk.** PHILIP A. KOBER (*J. Amer. Chem. Soc.*, 1913, 35, 1585—1593).—An improved form of nephelometer is described for the estimation of the proteins of milk by the formation of suspensoids with suitable reagents after the extraction of the fat (compare this vol., ii, 260, 355). The method, which greatly reduces the time usually necessary for such estimations, gives results which compare favourably with those of the processes at present in common use. D. F. T.

**The Quantitative Estimation of Tryptophan.** E. HERZFELD (*Biochem. Zeitsch.*, 1913, 56, 258—266).—The reagent used for this purpose consists of 20 grams of *p*-dimethylaminobenzaldehyde dissolved in a mixture of 500 c.c. of concentrated hydrochloric acid and 500 c.c. of water. To 50 c.c. of the solution to be tested, which contains tryptophan, are added 10 c.c. of this reagent, and the mixture is then diluted to 100 c.c. with concentrated hydrochloric acid. After thirty hours the colour is measured. (A distinct blue colour is obtained when the above mixture contains tryptophan to the extent of 1 part in 1,000,000.) The colour can be estimated approximately by comparison with an ammoniacal copper sulphate solution prepared in the following way. One gram of anhydrous copper sulphate is dissolved in 100 c.c. of water; 1 c.c. of this solution is mixed with 20 c.c. ammonia solution, and the mixture is diluted with water to 100 c.c. The colour thus obtained corresponds very nearly to that given with 0.0001 gram tryptophan with the aldehyde reagent. A more accurate way of ascertaining the amount of colour in a solution is the spectrophotometric method described in detail by the author. To estimate the tryptophan content of a protein, 1 gram of the substance is dissolved in 500 c.c. of 0.5% sodium carbonate solution, and incubated for twenty-four hours with 0.5 gram pancreatin (with known tryptophan content); 50 c.c. of the digest are then treated with the *p*-dimethyldiaminobenzaldehyde solution in the manner described above. A table is given showing the tryptophan content of various proteins. S. B. S.