Analytical Chemistry.

Qualitative Chemical Analysis. V. MACRI (*Boll. Chim. Farm.*, 1920, **59**, 385—389).—The author gives a scheme according to which the metals are detected approximately in the opposite order to that of the method commonly employed, one advantage of this procedure being that it allows of the use of fixed alkalis or their salts. [See *J. Soc. Chem. Ind.*, 1920, November.]

T. H. P.

The Analysis of Aqueous Solutions with the Aid of the Refractometer. MAX DE CRINIS (*Zeitsch. physiol. Chem.*, 1920, **110**, 254—265).—The refractive index of salt solutions which do not manifest the phenomenon of molecular attraction is in direct linear proportion to the percentage of the concentration of the salt in the solution. On establishing this relation between the refractive index and the concentration of a solution, it is possible to calculate the percentage of the concentration by means of the formula $y = (nD\bar{X}\% - 1\cdot 33320)/b$ ($nDX\%$ = refractive index of $X\%$ solution, b = refractive index of 1% solution of the same salt, $1\cdot 33320$ = refractive index of distilled water). The refractive index of a mixture of equal parts of various salt solutions is equal to the sum of the refractive indices of the solutions which make it up. If by mixing these salts some substance is precipitated, the refractive index of the precipitated salt can be obtained by subtracting the refractive index of the remaining solution from the sum of the refractive indices of the component solutions. The ion content of the aqueous solution can therefore be calculated, as follows: $P = (nDRX\% - nDOX\%)/K$. P = percentage; $nDRX\%$ = refractive index of $X\%$-solution obtained by calculation; $nDOX\%$ = refractive index observed after precipitation; $K = nDR1\% - nDO1\%$ of a 1% solution. S. S. Z.

A Simple Method for Titrating Electrometrically to a Desired End-point in Acid-alkaline Reactions. P. E. KLOPSTEG (*Science*, 1920, **52**, 18—19).—The hydrogen electrode can be utilised to compare a known standard solution with one of unknown p_H value. From the curves of Sörensen (*Ergebn. Physiol.*, 1912, **12**, 393) or the formulæ of Clark and Lubs (A., 1916, ii, 44) is selected the solution with p_H value corresponding with the point to which it is desired to titrate. This solution is placed in connexion (by means of a bridge of potassium chloride solution) with the unknown, each being provided with a hydrogen electrode. The two electrodes are connected by a tapping key and high-resistance galvanometer. Titration to an end-point is effected by merely adding solution until, on tapping the key, no deflection is observed, showing equal hydrogen-ion concentrations in the two solutions. The accuracy is limited by that of the p_H value of the standard solution. CHEMICAL ABSTRACTS.

The H-ion Concentration of some Standard Solutions at Various Temperatures. L. E. WALBUM (*Biochem. Zeitsch.*, 1920, **107**, 219—228; *Compt. rend. Soc. Biol.*, 1920, **83**, 707—709).—The H-ion concentration of mixtures of glycine and sodium hydroxide, borate and hydrochloric acid, and borate and sodium hydroxide increases with increased temperature between $10°$ and $70°$. The reverse is the case with a citrate and sodium hydroxide mixture. In the former three mixtures, the alteration is more marked in the alkaline mixtures, but diminishes with the diminution of the alkalinity of the mixtures S. S. Z.

Use of Ethyl Ether in Iodometric Estimations. L. GERET (*Mitt. Lebensmittelunters. Hyg.*, **11**, 67—68; from *Chem. Zentr.*, 1920, iv, 354).—Commercial ethyl ether can liberate large quantities of iodine in consequence of the presence of peroxidised substances. Such ether should be dehydrated with calcium chloride and subjected to prolonged treatment with metallic sodium, or shaken with concentrated alkali thiosulphate, rapidly dried over calcium chloride, and distilled.   H. W.

Extensive Employment of Arsenious Acid in Volumetric Analysis. R. NAMIAS (*Giorn. chim. ind. applicata*, 1920, **2**, 176).—A reply to de Bacho (this vol., ii, 188).

                                                CHEMICAL ABSTRACTS.

Application of the Thermal Conductivity Method to the Analysis of Complex Mixtures of Gases. E. R. WEAVER and P. E. PALMER (*J. Ind. Eng. Chem.*, 1920, **12**, 894—899).— The thermal conductivity method can only be applied quantitatively when the probable identity and amounts of constituents likely to be present in a gaseous mixture are known. For estimation of a constituent by comparison with a standard gas, air is the most suitable standard for mixtures with low conductivity, and hydrogen for those with high conductivity. This is suitable for estimating hydrogen in air, the relative proportions of hydrogen and ammonia in gases for synthetic ammonia processes, and impurities in hydrogen. In other cases, such as the estimation of chlorine, hydrogen chloride, sulphur dioxide, acetylene, and water vapour in various gaseous mixtures, the results are calculated by comparing the conductivities before and after a chemical reaction. Thus, the total amount of atmospheric gases in a hydrogen-filled balloon may be estimated by applying the method before and after the reaction of the oxygen with the hydrogen. Similarly, methane in air may be estimated by the difference in the results obtained before and after passing the air over hot copper oxide. Another modification is to add a gas to a mixture prior to the reaction. For example, in estimating oxygen in flue gas, hydrogen is first added, and the oxygen removed by combustion. The difference in the conductivities of the residual excess of hydrogen and nitrogen in the mixture is too small to affect the accuracy of the results for oxygen. In like manner, successive combustions with oxygen and hydrogen may be used for certain mixtures, as, for example, in estimating carbon monoxide in the presence of large amounts of hydrogen.   C. A. M.

Estimation of Chlorine in Blood. M. RODILLON (*Presse méd.*, **28**, 85—86; from *Chem. Zentr.*, 1920, iv, 315—316). —A solution of trichloroacetic acid (1 : 5 ; 15 c.c.) is added slowly and with stirring to an equal volume of the well-centrifuged serum, and the mixture is passed through a folded filter. 11·7 c.c. of the filtrate (a portion is reserved for the estimation of carbamide) are treated with $N/10$-silver solution (10 c.c.), distilled water

(50—60 c.c.), and finally with ferric alum solution (10 c.c.); the mixture is thoroughly agitated and titrated with $N/10$-ammonium thiocyanate solution until the red coloration persists.   H. W.

A New Method for the Estimation of Bromine. G. HARTWICH (*Biochem. Zeitsch.*, 1920, **107**, 202—206).—The urine is incinerated with sodium carbonate and acidified with sulphuric acid. Chlorine water is added and the liberated bromine is extracted with chloroform. The bromine is calculated from the quantity of chlorine used up. 347 Mg. of sodium bromide were estimated by this method in 100 c.c. of bromine-free urine with an error of about 3%.   S. S. Z.

Use of Barcroft's Differential Apparatus. R. WERTHEIMER (*Biochem. Zeitsch.*, 1920, **106**, 1—11).—Replacement of Barcroft's formula (A., 1908, ii, 319, 529) by that of Münzer and Neumann (A., 1917, i, 520) gives for the gas volume a value higher by about 0·5%, or, if the barometric pressure is corrected for the pressure of the water vapour, lower by about 0·4%. Use of Barcroft's formula and neglect of the water-vapour pressure correction is hence recommended. Determination of the constants of the apparatus is described.   T. H. P.

Investigations on Alveolar Gas Pressures by a New Method. PIUS SUPERSAXO (*Biochem. Zeitsch.*, 1920, **106**, 56—82). —The author has tested a new method, devised by Asher, for investigating alveolar air which permits of the estimation of both the carbon dioxide and the oxygen. The analysis is carried out by means of the Bunte burette, and as it requires 100 c.c. of air, Haldane and Priestley's method (A., 1905, ii, 400) is modified so as to yield increased quantities of the alveolar air. The method is fully described.   T. H. P.

Estimation of Neutral Sulphur in Urine. PAUL LIEBESNY (*Biochem. Zeitsch.*, 1920, **105**, 43—48).—Estimation of the sulphur in sulphosalicylic acid solution by precipitation as benzidine sulphate was found to yield results 8—10% in excess of the true value, owing to the presence of sulphur compounds in the gas employed as source of heat during the operations. The author has therefore modified Raiziss and Dubin's method of estimating the total sulphur in urine (A., 1914, ii, 671), use being made of an electric combustion furnace. The total sulphates in urine may be estimated by Rosenheim and Drummond's method (A., 1914, ii, 485), the difference between total sulphur and total sulphates representing neutral sulphur.   T. H. P.

Volumetric Method for the Estimation of Acids and Bases which yield Insoluble Salts. HANS TH. BUCHERER (*Zeitsch. anal. Chem.*, 1920, **59**, 297—302).—For the estimation of sulphuric acid, the hot solution containing the latter is titrated with N-barium chloride until the precipitation of barium

sulphate appears to be complete. A small portion of the solution is then filtered, and the filtrate divided into two portions, which are tested with a drop of barium chloride solution and a drop of dilute sulphuric acid respectively. If a precipitate is obtained with barium chloride, the titration is continued, and the solution again tested after filtration. In this way, the amount of barium chloride necessary for the precipitation of the sulphuric acid is ascertained approximately. The titration is then repeated on a fresh portion of the original solution, the final titration being made with $N/10$-barium chloride solution. Similar methods of titration may be used for the estimation of calcium (as oxalate), magnesium (as ammonium magnesium phosphate), etc.

W. P. S.

A Little-known Still-head for Kjeldahl Distillation. A. PRANGE (*Chem. Zeit.*, 1920, **44**, 681).—To guard against frothing over during distillation of ammonia when estimating nitrogen by the Kjeldahl process, the glass tube leading from the distillation flask to the receiver is inclined in an upward direction for some distance from the safety bulb. This gives additional security should the bulb become filled with froth. E. H. R.

The Technique for the Estimation of the Residual Nitrogen in Blood. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **101**, 62—73).—A theoretical paper. Folin and Wu's method (A., 1919, ii, 308) is considered an improvement on other methods.

S. S. Z.

Colorimetric Estimation of Ammonia, Nitrites, and Nitrates. I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 1253—1264).—In addition to the difficulty that colorimetric determinations are not accurate to within 5 to 10%, irregularities occur in practice from the influence of such factors as the quantity of reagent, the temperature, the time, the presence of retarding substances, etc. In the quantitative estimation of traces of ammonia by means of Winkler's reagent, which will detect 0.1 mg. NH_4 per litre, time was not found of great importance, the colour being at its maximum for different concentrations of the reagents after fifteen minutes in all cases. The quantity of reagent used has a marked effect, 0.3 c.c. of Winkler's reagent producing the same colour with 50 c.c. of a solution containing 0.6 mg. NH_4 per litre as 0.5 c.c. produced with the same volume of a solution containing 0.4 mg. NH_4 per litre. The strongest colour was obtained by adding 0.5 c.c. of the reagent to 50 c.c. of the ammoniacal solution. The presence of excess of potassium iodide depresses the sensitiveness enormously; the presence of 0.3 c.c. N-KI with 1 c.c. of the reagent and 50 c.c. of a solution containing 10 mg. NH_4 per litre reduced the colour to equality with that given by 50 c.c. of a solution containing 0.35 mg. NH_4 with 1 c.c. of the reagent, whilst 0.6 c.c. N-KI prevented the formation of the colour completely. The influence of a small excess of potassium

iodide varies with the concentration of the reagents. Bromides and thiocyanates have a preventive effect, although not so great as iodides. Chlorides have very little effect unless in large quantity. Sulphates have little effect on the colour, but hasten the separation of the orange precipitate. Secondary phosphates weaken the colour, whilst addition of excess of alkali hydroxide inhibits it entirely, as also does cyanide. A very satisfactory reagent, capable of detecting $0 \cdot 1$ mg. NH_4 per litre, is mercury sodium chloride in weak alkaline solution, which gives a white opalescence permitting of nephelometric estimation.

The recent work of Frederick (A., 1919, ii, 371) and Massink (*Water*, **3**, 89) on the phenol–sulphuric acid method of estimating nitrates is examined, and the influence of traces of chlorides shown by Massink to be necessary is confirmed, although the quantitative effect is greater than Massink stated. The test is best carried out by adding to the working solution $0 \cdot 5$ c.c. N-NaCl, evaporating to dryness, adding to the residue 2 c.c. of phenol-sulphuric acid, and warming for twenty minutes on the water-bath. The liquid is then diluted and rendered ammoniacal according to the procedure of Frederick. In the new form, the reaction is quantitative, the colour being proportional to the amount of nitrate present. Nitrites have very little effect on the reaction in this form. The brucine–sulphuric acid method was also examined, but no quantitative results could be obtained.

The Griess-Romijn method for the colorimetric determination of nitrite is also examined, and modifications are recommended. If 100 c.c. of the reagent be added to 50 c.c. of the solution under test, and the mixture warmed to 55—60° for five minutes, the maximum colour is reached at once on cooling. Since alkalis inhibit strongly, a hard water should first be made acid with acetic acid.   S. I. L.

Estimation of Ammonia in Urine, in Serous Liquids, and in the Oxidised Liquid of the Kjeldahl Method. ARNOLD HAHN and ELISABETH KOOTZ (*Biochem. Zeitsch.*, 1920, **105**, 220—228).—Using Hahn's modification of the Krüger, Reich, and Schittenhelm method, all the ammonia is expelled in five minutes from a solution containing $0 \cdot 04$ gram of ammonia as ammonium sulphate, 25 c.c. of water, 10 grams of sodium chloride, 1 gram of sodium carbonate, and 30 c.c. of 96% alcohol if the distillation flask is heated in a boiling-water bath and the distillation is carried out in the maximum vacuum given by a water pump. Under these conditions, carbamide (2 grams) yields no ammonia. Cooling of the receiver containing the standard acid for absorbing the ammonia is found to be unnecessary. Methods based on the above results are given for the estimation of ammonia in urine either free from, or containing, protein, in blood serum, and in the decolorised acid liquid of the Kjeldahl method. A special indicator containing sodium alizarinsulphonate and methylene-blue is used for titrating the alcoholic $N/100$-acid used in the case of blood serum.   T. H. P.

The Conductometric Titration of Phosphoric Acid and its Salts. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112,** 165—171).—Phosphoric acid behaves as a strong acid, and cannot be titrated conductometrically in concentrated solution (compare this vol., ii, 420). In dilute solution it can be titrated in exactly the same way as a mono- or di-basic acid, the first equivalent point being very sharp, the second less distinct. The conducto-metric method of titration has the advantage over the indicator method that indicators give indistinct end-points in very dilute solutions of phosphoric acid. Secondary phosphates, for example, Na_2HPO_4, can be titrated with acids when the concentration is less than 0·01 molar. When the concentration is greater, the break in the conductivity curve at the point corresponding with primary phosphate is indistinct, owing to the dissociation of phos-phoric acid. Secondary phosphates cannot be titrated with alkali, on account of the hydrolysis of the tertiary phosphates. Dilute solutions of pyrophosphates can be satisfactorily titrated with acid to the secondary salt. The break corresponding with the tertiary salt is indistinct. E. H. R.

Estimation of Carbon Dioxide in Alkali Hydrogen Carbonates in the Presence of Carbonates. WILHELM HARTMANN (*Zeitsch. anal. Chem.*, 1920, **59**, 289—297).—When a mixture of sodium hydrogen carbonate and sodium carbonate is mixed with 70% glycerol solution (7 c.c. for each 0·1 gram of carbonate) and heated at 115° for ten minutes, the whole of the carbon dioxide in the hydrogen carbonate is liberated, and, after being passed through suitable drying apparatus, may be collected in an ordinary potash bulb and weighed. At the end of the ten minutes the temperature should be lowered to 100°, and a current of air passed through the apparatus to convey the carbon dioxide into the potash bulb. If the same mixture is then heated at 190° for five minutes, two drops of water now added, and the heating continued for a further ten minutes, the carbonate is decomposed, and the resulting carbon dioxide may be collected and weighed. In most cases, the greater part of the water evolved with the carbon dioxide may be separated by means of a short reflux apparatus, but when ammonium salts are present, a vessel con-taining sulphuric acid must be used for drying the gas and removing the ammonia. W. P. S.

The Conductometric Estimation of Carbonic Acid and its Salts. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112,** 155—164).—Solutions of carbonic acid, from 0·0015 to 0·02 mol. in strength, can be titrated conductometrically with alkali. The conductivity straight-line curve becomes steeper after the form-ation of the hydrogen carbonate, and again steeper after the formation of the normal carbonate. The breaks in the curve, however, are not sharp, especially in very dilute solutions, in which, owing to the considerable hydrolysis of the carbonate, the

straight-line portions become rounded into a continuous curve The sharpness of the titration can be greatly increased by having present an excess of calcium salt (calcium chloride) to precipitate the carbonate as it is formed. Time must be allowed during the titration for the precipitation of the calcium carbonate.

Carbonic acid cannot be titrated with carbonate to the hydrogen carbonate conductometrically, because the angle between the two portions of the curve is too obtuse. On the other hand, carbonate can be titrated with acid. According to the dilution, the conductivity may fall (in dilute solution) or rise (in stronger solutions, above $0.1N$) up to the hydrogen carbonate point. From this point, which is not sharp, to the neutral point, the conductivity increases gradually, and at the neutral point there is a sharp rise. The neutral point is very sharp in extremely dilute solutions. Free alkali hydroxide can be estimated in presence of carbonate by titration with acid if not present in too small an amount. The amount of hydrogen carbonate in carbonate can be determined by titration with alkali or acid, but its amount must not be too small, or the direction of the corresponding portion of the curve cannot be determined with sufficient accuracy. A very weak acid, such as boric acid, can be titrated in presence of sodium carbonate with alkali hydroxide with satisfactory results.   E. H. R.

Microchemical Reactions of Radium ; its Differentiation from Barium by Iodic Acid. G. DENIGÈS (*Compt. rend.*, 1920, **171**, 633—635).—Radium salts give results identical with those of barium salts in the microchemical tests where hydrofluosilicic acid, oxalic acid, tartaric acid, potassium ferrocyanide, potassium tartrate, ammonium cyanurate, or ammonium phosphomolybdate in ammoniacal solution are used respectively as reagents. Iodic acid can be used, however, under certain conditions to differentiate between the salts of these two metals. If the concentration of the solution does not exceed 0.3%, radium and barium salts give typical and distinct microcrystalline precipitates with a 10% solution of iodic acid.   W. G.

Titrations with Surface-active Substances as Indicators. II. Estimation of Acidity with Capillary–active Substances of Alkaline Nature. WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **100**, 130—147. Compare this vol., ii, 48).—Salts of substances of an alkaline nature, such as quinine hydrochloride, veratrine hydrochloride, eucupine dihydrochloride, were used as indicators in acidimetric titrations, according to Traube's method, by changing the surface tension of the indicator. Eucupine dihydrochloride was found to be as sensitive as decoic acid is in alkalimetry. With this indicator, it is possible to carry out graduated titrations of a strongly dissociated acid in the presence of a primary phosphate in varying proportions. By this method, the amphoteric reaction of mixtures of primary and secondary phosphates can also be demonstrated.   S. S. Z.

Titrations with Surface-active Substances as Indicators. III. Investigation of Carbonates and Phosphate–Carbonate Mixtures by Utilising Surface-active Indicators of Acid and Alkaline Nature. Wilhelm Windisch and Walther Dietrich (*Biochem. Zeitsch.*, 1919, **101**, 82—109. Compare this vol., ii, 48, and preceding abstract).—The carbonates and hydrogen carbonates of potassium and sodium react alkaline with eucupine dihydrochloride as a surface tension indicator; those of magnesium react less alkaline than the above, but more alkaline than calcium normal and hydrogen carbonates. When these carbonates are mixed with primary potassium phosphate in the cold, the two substances react until a certain equilibrium is attained, showing the same order of alkalinity as the above. This is obtained with the alkaline surface tension indicator, eucupine dihydrochloride, as well as with the acid surface tension indicator, sodium undecoate. When heated, the alkali carbonates have the same influence on the primary phosphate as alkali hydroxide. The action of magnesium and calcium hydrogen carbonates on the primary phosphate under these conditions is complicated. The alkaline action of the alkaline earth hydrogen carbonates is proportionately greater when small quantities are used than when larger ones are employed.

S. S. Z.

Estimation of Potassium as Perchlorate, and the Separation from Sodium, etc. R. Leitch Morris (*Analyst*, 1920, **45**, 349—368).—A critical examination of the perchlorate method for the estimation of potassium, together with suggestions as to the most suitable forms of apparatus. The potassium salt solution should be evaporated three times with perchloric acid, and in the final evaporation taken practically to dryness. The residue is treated with 10 c.c. of wash liquid (100 c.c. of 98% by vol. alcohol and 1 c.c. of 20% perchloric acid), stirred occasionally for fifteen minutes when sodium is present and the liquid then decanted through a weighed Gooch crucible containing asbestos. When only potassium is present, the precipitate is rinsed directly on to the filter with a small, measured quantity of the wash liquid. If sodium is present, the basin containing the precipitate from the first decantation is heated slightly to evaporate the alcohol, the precipitate dissolved in a small quantity of water, the solution evaporated to dryness, the precipitate treated with 10 c.c. of wash liquid, the latter decanted on to the filter, and the precipitate transferred by using 10 c.c. of the filtrate. Finally, the precipitate is washed on the filter by a measured volume of wash liquid, the crucible and its contents dried at 130° to 150° for one hour, cooled in a desiccator for one hour, and weighed. The weight is taken as being constant when, on washing with 3 c.c. of liquid, the difference between successive weighings does not exceed 0·2 mg. When much phosphoric acid is present, the evaporation with perchloric acid should not be to dryness, but to a moist, pasty condition; the residue is then treated with 15 c.c. of 98% alcohol. and finally washed with the wash liquid. Calcium, iron,

aluminium, and barium do not interfere, and magnesium is also
without effect provided that the evaporation with perchloric acid
is not carried to dryness. Organic acids tend to char during the
evaporation, and when they are present it would seem preferable
to separate the potassium previously by the cobaltinitrite method.
In the case of sulphates, the sulphuric acid should be removed by
treatment with barium chloride, but it is not necessary to remove
the slight excess of barium chloride used.   W. P. S.

The Precipitation of the Calcium Group and Magnesium.
I. M. KOLTHOFF (*Pharm. Weekblad*, 1920, **57**, 1229—1234).—The
sensitiveness of ammonium carbonate, as usually used for the pre-
cipitation of Group IV in presence of ammonium chloride, leaves
much to be desired. Ammonium carbonate in the cold gives no
precipitate with solutions containing less than 25 mg. of calcium
per litre, and at that concentration the precipitate is visible only
after fifteen minutes. The sensitiveness is greater at the boiling
point; in presence of free ammonia, a concentration of 5 mg.
of calcium per litre, shows a precipitate in boiling ammoniacal
solution. Ammonium chloride renders the reaction much less
sensitive. The same conclusions are found to hold for strontium
and barium, the latter being least sensitive to ammonium
carbonate, as would be expected from the solubilities of the
Group IV metal carbonates.

Sodium carbonate is found to be a much more sensitive reagent,
giving precipitates at the boiling point from solutions containing
only 1 mg. of calcium, 3 mg. of strontium, or 5 mg. of barium per
litre. The use of sodium hydroxide and carbonate together is
recommended to ensure complete precipitation of magnesium, which
can be removed by the chromate method and reprecipitated with
ammonium phosphate. Considerable excess of these reagents is
not harmful to the reaction, as the ammonia set free from the
ammonium chloride present has no tendency to prevent
precipitation of the magnesium.   S. I. L.

**Estimation of Calcium and Magnesium in Different
Saline Solutions.** E. CANALS (*Compt. rend.*, 1920, **171**,
516—518).—If to a solution containing calcium, magnesium, iron,
and aluminium salts, just acidified with sulphuric acid, sodium
phosphate is added and the solution made alkaline with ammonium
hydroxide, it is possible to retain the whole of the calcium and
magnesium in solution by acidifying with acetic acid and shaking
vigorously for several minutes.   W. G.

Detection of Magnesium. FRITZ EISENLOHR (*Ber.*, 1920, **53**,
[*B*], 1476—1477).—Five c.c. of a solution of alkannin in alcohol
(96%) are treated with a drop of 2*N*-ammonium carbonate solution,
which does not cause any change in colour, and then with a drop of
the neutral salt solution; the presence of magnesium, strontium, or
manganese is denoted by the development of a bluish-violet colora-
tion which becomes pale red after acidification with one or at most
two drops of 2*N*-hydrochloric acid; subsequent addition of the

same number of drops of $2N$-ammonium carbonate solution restores the bluish-violet colour only if magnesium is present. If the latter is present as magnesium ammonium phosphate, the salt is dissolved in $2N$-hydrochloric acid, and a drop of this solution is added to the alkannin tincture; further addition of 1—2 drops of ammonium carbonate causes the appearance of the bluish-violet colour if magnesium is actually present, whilst otherwise the original colour of the tincture is restored. It is essential that the alcoholic solution should not become diluted with water, since in this case the ammonia hydrolytically produced gives a blue coloration. H. W.

The Acidimetric Estimation of Heavy Metals in their Salts. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 172—186).—Experiments were made to determine with what degree of accuracy the salts of heavy metals which form insoluble hydroxides can be titrated with alkali hydroxides, either by the conductometric method or with the help of indicators. The statement of Harned (A., 1917, ii, 272) that magnesium sulphate can be estimated conductometrically by titration with barium hydroxide was confirmed. Satisfactory results were also obtained by precipitating the magnesium hydroxide with excess of standard alkali, filtering, and titrating back with standard acid. The conductometric method gave unsatisfactory results when zinc sulphate was titrated with sodium or barium hydroxide, owing to the precipitation of basic salt. Better results were obtained by titrating sodium hydroxide with zinc sulphate. In the case of copper sulphate also, the formation of basic salt interferes with the titration, and satisfactory results could not be obtained. Mercuric chloride can be titrated conductometrically with accuracy by running the solution into sodium hydroxide solution, which should not be stronger than $0.01N$. In the case of aluminium salts, when these are titrated with sodium or barium hydroxide, a sharp break in the conductivity curve is not obtained at the neutral point, but there is a very sharp break at the point where the formation of aluminate is complete. Aluminium hydroxide behaves, therefore, as a mono-basic acid. Aluminium sulphate or alum can be titrated with sodium hydroxide at the boiling temperature in presence of excess of barium nitrate, using phenolphthalein as indicator. Slight excess of alkali is run in and titrated back with acid. The results are accurate.

E. H. R.

Use of Diphenyl Derivatives in Qualitative Analysis. F. FEIGL (*Chem. Zeit.*, 1920, **44**, 689—690).—Benzidine and other diphenyl derivatives yield intense blue colorations with manganic, ceric, cobaltic, and thallic compounds. For the detection of traces of the latter their solution is rendered alkaline with sodium hydroxide solution prepared with ordinary tap water (the presence of calcium carbonate is advantageous since it occludes the traces of metallic hydroxides), the mixture filtered, and the filter then treated with a drop of benzidine acetate solution. The test will detect the presence of 1 part of manganese in 125 million parts of

solution. Thallic compounds even give a blue coloration with the reagent without previous treatment with alkali; cobalt salts must be heated with alkali solution to obtain the pink hydroxide before the reaction with benzidine can be obtained. In the case of iron the blue coloration is not obtained when all the iron has been precipitated from solution by alkali. W. P. S.

Electro-analytical Separation of Nickel (Cobalt) from Arsenic. N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1920, **42**, 1789—1793).—Nickel may be quantitatively separated from salts of arsenic acid in ammoniacal solution by the electric current. Cobalt on deposition carries down arsenic, whereas the nickel precipitate is free from arsenic. If the two metals are deposited simultaneously, arsenic may or may not be deposited, according to the conditions. J. R. P.

Volumetric Methods for Estimating Tin. J. G. F. DRUCE (*Chem. News*, 1920, **121**, 173—175).—Stannous tin may be more accurately estimated by a volumetric method in an acid solution. Titration with standard iodine solution in the presence of hydrochloric acid gives satisfactory results with stannous chloride, inorganic stannochlorides, and stannochlorides of aliphatic amines, but is less suitable for aromatic amine compounds, which have a tendency to darken during the titration, and so obscure the end-point. For the titration of stannous chloride with potassium permanganate solution, the hydrochloric acid should be kept as low as possible by dissolving the salt in dilute sulphuric acid, and titrating the solution as rapidly as possible. Potassium dichromate is usually less trustworthy as a reagent for the titration. C. A. M.

Estimation of Zirconium. MELVIN S. SMITH and C. JAMES (*J. Amer. Chem. Soc.*, 1920, **42**, 1764—1770).—Zirconium is precipitated by selenious acid from a boiling solution acidified with hydrochloric acid. The basic selenite on ignition leaves zirconia. It is shown that this method gives satisfactory results in the estimation of zirconium in a pure salt, in the separation of zirconium from aluminium and rare earths, and from iron when the amount of ferric oxide in the combined oxides of iron and zirconium does not exceed 10%. Titanium is precipitated with zirconium, and a correction must be applied in this case or the precipitation carried out in presence of excess of hydrogen peroxide, when zirconium alone is precipitated. If phosphates are present the zirconium phosphate in the ammonia precipitate is insoluble in hydrochloric acid, and must be fused with sodium carbonate, boiled with water, and the residue dissolved in hydrochloric acid and added to the main solution. A method for the analysis of zirconia ore is described. J. R. P.

Estimation of Antimony in Lead–Antimony Alloys. L. BERTIAUX (*Ann. Chim. anal.*, 1920, [ii], **2**, 273—278; *Bull. Soc. chim.*, 1920, [iv], **27**, 769—771; *Chim. et Ind.*, 1920, **4**, 467—472). The alloy is dissolved by heating with sulphuric acid and

sodium sulphate, the solution is diluted with water, hydrochloric acid, and a few drops of a 0·1% solution of Poirrier's orange, and the mixture is titrated with standardised permanganate solution until the colour is just discharged. The hydrochloric acid keeps the antimony sulphate in solution, and as soon as all the antimony has been oxidised by the permanganate the next drop of permanganate solution introduced reacts with the hydrochloric acid, liberating chlorine, which decolorises the Poirrier's orange. Bismuth, copper, tin, and arsenic do not interfere; iron is titrated together with the antimony, but its quantity may be estimated colorimetrically with thiocyanate in the solution in which the antimony has been titrated. [See, further, *J. Soc. Chem. Ind.*, 1920, 693a.] W. P. S.

Sensitive Modification of Lieben's Reaction for Iodoform. RUDOLF KUNZ (*Zeitsch. anal. Chem.*, 1920, **59**, 302—303).—For the detection of traces of alcohol by this test, 10 c.c. of the solution are treated with 2 c.c. of 10% sodium hydroxide solution, 0·15 gram of potassium iodide and 0·2 gram of potassium persulphate, and the mixture is heated at 60°. A solution containing one drop of alcohol in 100 c.c. of water yields a turbidity, due to the formation of iodoform, within ten minutes. W. P. S.

The Conductometric Titration of Phenols. I. M. KOLTHOFF (*Zeitsch. anorg. Chem.*, 1920, **112**, 187—195).—Phenol and the cresols can be accurately titrated conductometrically with alkali in 0·1 or 0·01N-solution. Vanillin and sodium phenolsulphonate can be similarly titrated. In salicylic acid the hydroxyl group loses its acidic character and cannot be titrated, but its esters, for example, salol or methyl salicylate, can be accurately titrated as phenols; *p*-hydroxybenzoic acid behaves as a dibasic acid. Thymol and β-naphthol are also satisfactorily titrated. Of the dihydroxy-benzenes, catechol behaves as a monobasic acid, the conductivity curve showing only one break, corresponding with the first hydroxyl group; quinol behaves as a dibasic acid, the first break not being very distinct, whilst resorcinol, which also behaves as a dibasic acid, gives better results when titrated with barium instead of sodium hydroxide. Pyrogallol functions as a dibasic acid, not monobasic, as stated by Thiel and Roemer (A., 1908, i, 787, 791), and so does phloroglucinol, whilst gallic acid, having a carboxyl in addition to three hydroxyl groups, behaves as a tribasic acid.
E. H. R.

Estimation of Terpin. OBDULIO FERNÁNDEZ and N. LUENGO (*Anal. Fis. Quim.*, 1920, **18**, 158—165).—When terpin is treated with acetic anhydride and anhydrous sodium acetate, only one of its two hydroxyl groups is acetylated; hence it behaves like a monohydric alcohol, although the results are slightly high. When a small quantity of sulphuric acid is used instead of sodium acetate, the reaction takes place spontaneously, and one hydroxyl group is acetylated. The quantity of acetic anhydride required is two to three times that of the terpin, the mixture being left for

one or two hours. Complete esterification is achieved by Boulez's method (A., 1907, ii, 306): 5 grams of terpin are dissolved in 25 grams of rectified oil of turpentine and 40 grams of acetic anhydride. Three grams of fused sodium acetate are added, and the mixture boiled for three hours. The liquid is digested for twenty minutes on the water-bath with a little water, and a saturated salt solution added; the top layer is made up to 100 c.c. with oil of turpentine and dehydrated with calcined sodium sulphate; an aliquot part of the liquid is then hydrolysed with alcoholic $N/2$-sodium hydroxide solution.   W. R. S.

An Accelerated Method of Estimating the Reducing Values of Cellulosic Substances. E. KNECHT and L. THOMPSON (*J. Soc. Dyers and Col.*, 1920, **36**, 255—257).—Schwalbe's method for estimating the copper number of oxycellulose is modified by adding the cuprous oxide to a ferric salt solution and titrating the ferrous salt so formed with potassium permanganate. By this means it is unnecessary to determine the unreduced copper absorbed by the cellulose (copper hydroxide number), which is the difference between the above number and that obtained from an estimation of the unreduced copper in the filtrate by titanous chloride.

The copper number may be determined by a process based on the fact that oxycellulose precipitates cuprous thiocyanate from solutions of the cupric salt. This method avoids the errors that the action of the alkali hydroxide in Fehling's solution on oxycellulose may cause.

The copper number may also be determined by heating oxycellulose with sodium hydroxide and rosinduline, and then titrating with titanous chloride to determine the amount of dye reduced.

All three methods give sufficiently accurate results, and are more quickly carried out than the original Schwalbe method. [See *J. Soc. Chem. Ind.*, 1920, 718A.]   A. J. H.

Estimation of Acetic Anhydride. KNUT WOLGAST (*Svensk Kem. Tidskrift*, 1920, **32**, 110).—Twenty-five c.c. of acetic anhydride are dissolved in 30 c.c. of benzene, 25 c.c. of water are added, and after vigorously shaking for fifteen seconds the aqueous layer is drawn off and measured. The increase in volume is due to the acetic acid present, and multiplied by 4 gives the percentage of acetic acid. Some small amount of acetic anhydride will dissolve in water and some of the dilute acetic acid will dissolve in the benzene. A table of corrections is necessary In the following pairs of figures the first is the burette reading of increased volume multiplied by 4 and the second the corrected percentage: 93·5—100, 90—95·6, 85—89·6, 80—81·5, 75—75·8, 55—55·1, 50—50·1, 35—33·3, 25—21·7, 20—15·5, 11—0.   CHEMICAL ABSTRACTS.

Colour Test for Oxalic Acid. LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1920, **42**, 1784—1785).—A few crystals of resorcinol are dissolved in 5 c.c. of the solution by warming gently. The

liquid is cooled and an equal volume of concentrated sulphuric acid slowly poured in to form a layer. A blue ring is formed at the junction of the layers if oxalic acid is present. If the blue colour does not appear, the liquids are mixed by shaking, and, after cooling somewhat, another 5 c.c. of sulphuric acid added. If the colour still fails to appear, the liquid is warmed over a flame (not boiled), when an indigo-blue colour appears. If the mixture is boiled the colour becomes dark green. J. R. P.

Detection of Coumarin in Vanillin. L. GERET (*Mitt. Lebensm. Hyg.*, 1920, **11**, 69—71).—Five % of coumarin in vanillin can be detected by the yellow turbidity produced by the addition of a 1% solution of iodine in 2% potassium iodide solution; the turbidity changes to lustrous, metallic, bluish-black crystals containing 46·47% of iodine and yielding 13·36% of ash.

CHEMICAL ABSTRACTS.

Estimation of Aminoethyl Alcohol and of Choline appearing on the Hydrolysis of Phosphatides. P. A. LEVENE and T. INGVALDSEN (*J. Biol. Chem.*, 1920, **43**, 355—378).—The method is a modification of that introduced by Thierfelder and Schulze (A., 1916, i, 548). This method is employed in the original form up to the point where the free aminoethyl alcohol is extracted. This is accomplished by boiling the mixture of the hydrochlorides of the two bases and an excess of calcium oxide with dry acetone. The combined acetone extracts are acidified with hydrochloric acid, and evaporated in a vacuum. The residue is dissolved in water, evaporated to a syrup, and again treated with calcium hydroxide and acetone. The final acetone extracts are filtered, made acid with hydrochloric acid, and the acetone removed by vacuum evaporation.

The residue from the acetone extracts is treated with water and filtered from calcium hydroxide. Hydrochloric acid and the residual calcium are removed by silver oxide and carbon dioxide respectively. The choline is precipitated as picrate.

In an actual experiment on the separation of the bases from the ether-soluble, acetone-insoluble lipoids from egg, 77·5% of the amino-nitrogen was found present in the acetone extracts, whilst the yield of choline was 98·7% of the theory. J. C. D.

Separation and Estimation of Phenylalanine. SHINTARO KODAMA (*J. Tokyo Chem. Soc.*, 1920, **41**, 479—495).—In the ester or the lime method glutamic acid, aspartic acid, and phenylalanine are collected in the same fraction. The author adds lime to the mixture of the products of hydrolysis of a protein, whereby basic calcium glutamate is precipitated. The calcium salts subsequently obtained by concentrating the filtrate are washed with water or lime-water, heated with 7 to 8 volumes of water, and treated with carbon dioxide, whereby calcium carbonate is precipitated. When this filtrate is concentrated, phenylalanine crystallises.

An approximate estimation of the phenylalanine in a mixture of the calcium salts of phenylalanine (Ca, 9·98; H_2O, 8·91%), glutamic

acid (Ca, $16\cdot80$; H_2O, $22\cdot56\%$), and aspartic acid (Ca, $16\cdot51$; H_2O, $29\cdot63\%$) can be made if the percentage of calcium and of water of crystallisation is estimated.   By suspending the mixture in hot water and treatment with carbon dioxide, calcium glutamate and aspartate lose one-half of their calcium, and are converted into easily soluble, normal calcium salts, whilst the calcium salt of phenylalanine loses the whole of its calcium, and is converted into the free acid. The difference between the amount of calcium in the precipitate and in the solution corresponds with the amount of calcium originally combined with phenylalanine.

Several methods of obtaining perfumes from phenylalanine are described.   CHEMICAL ABSTRACTS.

Estimation of Taurine in Muscle. Y. OKUDA and KEIICHI SANADA (*J. Coll. Agr. Imp. Univ. Tokyo*, 1919, **7**, 77—80).—Sulphur is estimated in an aqueous extract of the muscle, after removal of all compounds of sulphur except taurine, for example, proteins, sulphates, and cystine (if necessary). The flesh (5 grams if fresh, 1 gram if dry) is ground and extracted first with cold water, then with warm water. The total extract is boiled with the addition of acetic acid; the coagulum is removed; the filtrate is neutralised, and is precipitated with basic lead acetate, an excess of that reagent being avoided.   The precipitate is removed by filtration; the filtrate is treated with sulphuric acid to precipitate the excess of lead; excess of sulphuric acid is removed with baryta, and excess of baryta with ammonium carbonate. The final filtrate is used for the estimation of sulphur, which is converted into sulphate and weighed as barium sulphate. Multiplication of the weight of barium sulphate by the factor $0\cdot5358$ gives the weight of taurine. Cystine is usually absent from the extract; if it is present, the above technique is modified; after precipitation of the excess of lead, more sulphuric acid is added until its concentration reaches 5%; the cystine is then precipitated with phosphotungstic acid and removed by filtration after remaining for two or three days. Treatment with baryta and with ammonium carbonate and estimation of taurine sulphur are made as usual. The percentage of taurine in fresh flesh and. in parentheses, in dry flesh, was: shark, $0\cdot13$ ($0\cdot61$); carp, $0\cdot13$ ($0\cdot61$); ordinary flesh of bonito, $0\cdot08$ ($0\cdot30$); " chiai " flesh of bonito, $0\cdot42$ ($1\cdot56$); *Neptunus pelagicus*, $0\cdot28$ ($1\cdot37$); *Palinurus vulgaris*, $0\cdot17$ ($0\cdot76$); *Pinna japonica* (adductor muscle), $0\cdot54$ ($2\cdot38$); *Avicula martensii* (mantle), $0\cdot91$ ($5\cdot20$).   All the samples of muscle (fish, mollusc, and crustacean) examined contained taurine; that compound was most abundant in molluscs, and less abundant in fish, although present in comparatively large amount in their " chiai " flesh.   CHEMICAL ABSTRACTS.

Detection of Cyanic Acid. R. FOSSE (*Compt. rend.*, 1920, **171**, 635—637).—The cyanic acid may be detected directly as such or after its conversion into silver cyanate.   In the first case a portion of the solution is heated for one hour with ammonium chloride, and the carbamide present in 2 c.c. of the solution thus

treated and in 2 c.c. of the untreated solution is estimated by means of xanthhydrol. An increase in the carbamide content of the solution by heating with ammonium chloride is evidence of the presence of cyanic acid. In the second case the silver cyanate is heated with ammonium chloride, and the resulting liquid tested for carbamide as above. Another portion of the silver cyanate is first heated with nitric acid and then with ammonium chloride, but in this case there is no formation of carbamide. W. G.

Volumetric Estimation of Thiocyanate by Potassium Permanganate. R. MEURICE (*Ann. Chim. anal.*, 1920, [ii], **2,** 272—273).—Trustworthy results are obtained when the thiocyanate solution is acidified with sulphuric acid, treated with an excess of standardised potassium permanganate solution, and the excess of the latter then titrated with dilute hydrogen peroxide solution. The excess of permanganate added should be at least one-half of that required for the oxidation of the thiocyanate. Direct titration of thiocyanate in acid solution with permanganate yields low results. W. P. S.

Detection of Hydrogen Cyanide. JAMES MOIR (*J. S. African Assoc. Anal. Chem.*, 1920, **3**, 16. Compare P., 1910, **26**, 115).— Filter paper is moistened with a reagent consisting of *o*-tolidine 1 gram, copper acetate 1·5 grams, glacial acetic acid 0·5 gram, and water 100 c.c., and is then suspended in the atmosphere to be tested. A blue colour appears on the paper if the air contains as little as 1 part of hydrogen cyanide in 2 millions. W. P. S.

Preparation of Phosphomolybdic Acid and its Application to the Colorimetric Estimation of Uric Acid. P. PROSCHOWSKY (*Kongl. Vet. Landbohöjskole Aarskrift*, 1918, 372—407; from *Chem. Zentr.*, 1920, iv, 315).—The author reviews the colorimetric methods which have been proposed for the estimation of uric acid in urine, and indicates a new procedure for the preparation of phosphomolybdic acid required in Höst's process; the latter has been examined in detail, and certain improvements are recommended. H. W.

Nuclein Metabolism. IX. Detection and Estimation of Combined and Free Purines in Human Blood and Pus Serum. S. I. THANNHAUSER and G. CZONICZER (*Zeitsch. physiol. Chem.*, 1920, **110**, 307—320. Compare A., 1919, i, 228).—For the estimation of the free purines in blood the serum is diluted with water and precipitated with 1·55% uranium acetate. The filtrate is boiled with some sodium acetate and sodium hydrogen sulphite and precipitated with 10% copper sulphate. The precipitate is centrifuged, washed, and the nitrogen in it is determined by the micro-Kjeldahl method. From the value obtained, the free purine content is calculated. The figures of the uric acid content of serum obtained by the colorimetric method and by the above method agree fairly well, and it is therefore to be concluded that only very

small quantities of free purines other than uric acid are present in the blood. In order to estimate the combined purines (nucleotides) in the blood, the diluted serum is boiled, and precipitated with a 20% solution of sulphosalicylic acid in order to remove the proteins. The filtrate is concentrated and the purines are precipitated with copper sulphate as previously described, and the total purines are obtained from the nitrogen estimation, whilst the combined purines are calculated by difference. One hundred c.c. of normal human serum contain 2—3 mg. of nucleotide nitrogen and 1—1·5 mg. of free purine nitrogen.   S. S. Z.

Colorimetric Estimation of Adrenaline. WILBUR L. SCOVILLE (*J. Ind. Eng. Chem.*, 1920, **12**, 769—771).—A mixture of 20 c.c. of water, 5 c.c. of 1% potassium iodate solution, and 0·25 c.c. of $N/1$-hydrochloric acid is heated at 38°, and 0·5 c.c. of a 0·1% solution of the sample is added. A similar mixture is prepared, but using 0·5 c.c. of pure adrenaline solution. Both mixtures are kept at 38° for fifteen minutes, then cooled, and the colorations compared. If the coloration of the test solution differs by more than 25% from that of the standard, the estimation should be repeated, using more or less of the solution. The pure adrenaline solution is prepared by dissolving 0·5 gram of the substance in 0·5 c.c. of $N/1$-hydrochloric acid and diluting the solution to 50 c.c.; if the solution to be examined contains sodium hydrogen sulphite, 0·05 gram of the latter should be added to the standard solution.   W. P. S.

Important Source of Error in the Examination of Urine for Albumin with Sulphosalicylic Acid. GRETE LASCH and JOSEF REITSTOETTER (*Münch. med. Woch.*, 1920, **67**, 484—485; from *Chem. Zentr.*, 1920, iv, 30).—Schall's assumption (this vol., ii, 398) that sulphosalicylic acid forms a precipitate with calcium chloride which can be mistaken for a precipitation of albumin is untenable.   H. W.

Detection of Slight Traces of Hæmoglobin in Urine. J. PITICARIU (*Compt. rend. Soc. Biol.*, 1920, **83**, 605—607; from *Chem. Zentr.*, 1920, iv, 31).—Spectroscopic examination of perfectly fresh urines which contain traces of hæmoglobin and to which Ehrlich's reagent (dimethylaminobenzaldehyde + hydrochloric acid) has been added, shows the characteristic absorption bands of oxyhæmoglobin at dilutions at which this is otherwise not the case.   H. W.

[Quantitative Comparison of] Vitamine Content. WALTER H. EDDY and HELEN C. STEVENSON (*J. Biol. Chem.*, 1920, **43**, 295—309).—The methods proposed by Bachmann (A., 1919, i, 613) and by Williams (A., 1919, i, 463) have been used for quantitative studies on the vitamine-*B*. A new technique is described which eliminates some of the difficulties in the manipulation of these two tests. It is shown that this method may be utilised in estimating the vitamine content of food.   J. C. D.