

Analytical Chemistry.

The Process of Preparation of Charcoal Sticks for Reduction. NESTOR C. ALEXANDRESCU (*Bull. Soc. chim. România*, 1919, **1**, 11—12).—The following process for the preparation of charcoal sticks for the reduction test in qualitative analysis is advocated. Thin wood chips, such as are used in match making, are boiled for two minutes in a 2.5% solution of ammonium phosphate, and then dried at a temperature not exceeding 60°. When it is required to carry out the test, half the stick is burnt, and then the test is carried out in the usual manner on the substance previously mixed with sodium carbonate. W. G.

Titration with Surface-active Substances as Indicators. Estimations of Acidity with the Homologues of the Fatty Acids Series. WILHELM WINDISCH and WALTHER DIETRICH (*Biochem. Zeitsch.*, 1919, **97**, 135—156).—Adopting Traube and Somogyi's method (A., 1915, ii, 101) of estimating the reaction by means of the alteration in the surface tension brought about by the displacement of the acid or the base of the indicator by the acid or base of the medium, the authors tried the homologues of the salts of the fatty acids series up to undecylic acid as indicators. The acids with C_9 — C_{11} have been found to be as sensitive as litmus and neutral-red. Free acids can be estimated in the presence of a primary phosphate by using the above acids as indicators.

S. S. Z.

A Considerable Source of Error in Titrations in the Presence of Phenolphthalein. HAEÜSSERMANN (*Süddentech. Apoth. Zeit.*, 1919, **59**, 361—362; from *Chem. Zentr.*, 1919, iv, 396).—The author directs attention to the errors, caused by the presence of free carbon dioxide in distilled water, which occur in titrations in which phenolphthalein is used as indicator. H. W.

Preparation of Phenolphthalein Solution and Paper without the Use of Alcohol. H. CLAASSEN (*Zentr. Zuckerind.*, **26**, 209; *Arch. Suikerind.*, 1919, **26**, 1588—1590).—When alcohol is unavailable, an indicator solution may be prepared by dissolving 1 gram of phenolphthalein in 12.5 c.c. of *N*-sodium hydroxide, and diluting to 500 c.c. with water. The alkali content of the solution is so small that it can be disregarded in factory work. Where greater accuracy is required, the result can be corrected for the alkalinity of the indicator. Test paper can be prepared by immersing paper first in a solution made by diluting 200 c.c. of the above indicator solution to 1 litre, drying, immersing it in a solution of sulphuric acid of the proper strength to give the desired acidity, and drying again. The results obtained with the paper should be verified from time to time by direct titration.

CHEMICAL ABSTRACTS.

Estimation of Bromine in Mineral Waters and Brines. W. F. BAUGHMAN and W. W. SKINNER (*J. Ind. Eng. Chem.*, 1919, **11**, 954—959).—Chromic acid liberates bromine from bromides quantitatively at the ordinary temperature, and the bromine may be removed by aspiration. Chlorides under the same conditions yield only a trace of chlorine, which probably forms chromyl chloride and remains in solution. When a mixture of chlorides and bromides is treated with the reagent, some chlorobromide is formed, and is removed, together with the bromine, on aspiration. In the method of analysis described, the residue from the mineral water is oxidised with chromic acid, with the addition of hydrogen peroxide, and the liberated halogens absorbed in a solution of sodium sulphite and carbonate. This is evaporated, and the residue

again oxidised with chromic acid, and a current of air aspirated through the apparatus, the absorption vessels of which contain potassium iodide solution. In this second aspiration the quantity of chlorine present is so small that only pure bromine is evolved, and its amount is found by titration of the liberated iodine. [See also *J. Soc. Chem. Ind.*, 1920, 19A.] C. A. M.

Test Paper for the Detection of Iodine. ANONYMOUS (*J. Pharm. Belg.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], 1, 357).—One gram of starch is mixed with 10 c.c. of water, 40 c.c. of boiling water are added, the mixture is boiled for two minutes, and 0.5 gram of sodium nitrite is then added. The paste obtained is painted on strips of paper by means of a brush, and the strips are dried. To make the test, a few drops of the solution under examination are poured on the paper, followed by one drop of dilute sulphuric acid. A blue coloration is obtained if the solution contains iodide. The test paper keeps well. W. P. S.

The Spectrocomparator, an Apparatus for the Estimation of the Percentage Saturation of Blood with Oxygen or Carbon Monoxide. AUGUST KROGH (*J. Physiol.*, 1919, 52, 281—287; from *Chem. Zentr.*, 1919, iv, 210—211).—A modification of Hartridge's method (*A.*, 1912, ii, 488) is proposed which gives satisfactory results and only requires small amounts of blood. The apparatus is fully described and figured in the original, which must be consulted for details. H. W.

Method for bringing Elementary Sulphur into Solution for Analysis. A. P. BJERREGAARD (*J. Ind. Eng. Chem.*, 1919, 11, 1055).—The finely divided sulphur is dissolved in a small quantity of dry bromine, nitric acid is added, and the mixture heated. The oxidation requires a few minutes only; after the excess of bromine has been expelled, the mixture is diluted with water, boiled with the addition of hydrochloric acid to expel nitric acid, and the sulphuric acid is then precipitated in the usual way as barium sulphate. W. P. S.

Non-protein Sulphur of the Blood. M. KAHN (*Proc. Soc. Exp. Biol. Med.*, 1919, 16, 139; from *Physiol. Abstr.*, 1919, 4, 374).—A method of fractionating and estimating the non-protein sulphur of the blood is described. J. C. D.

The Titration of Sodium Thiosulphate Solutions. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, 56, 644—657).—The preparation, testing, and application of various substances for the standardisation of thiosulphate solutions are described in detail, and their relative merits for the purpose discussed. The purest forms of potassium dichromate obtainable commercially contain free chromic acid or potassium chromate. A method for the detection and estimation of these is given which depends on the location of a discontinuity in the conductivity curve on the addition of alkali or acid.

If chromic acid is present the addition of standard alkali causes no increase in the conductivity of a dichromate solution until the free acid is neutralised. Similarly, no increase in conductivity is observed on the addition of acid to a solution containing chromate until all the latter has been converted into dichromate. For analytical purposes it is recommended to melt the pure dichromate in an electric furnace before use. The other substances examined are iodine, oxalic acid, cyanogen iodide, potassium iodate, and potassium bromate. All these are easily purified, and give results in the titration of thiosulphate with an error of less than 0.1%. The greatest error, 0.07%, was observed in titrating with dichromate.

W. S. M.

Influence of the Position of Substituents on the Behaviour of Aromatic Nitro-compounds in the Kjeldahl Estimation of Nitrogen. B. M. MARGOSCHES and ERWIN VOGEL (*Ber.*, 1919, 52, [B], 1992—1998).—The behaviour of the isomeric nitrophenols, nitrobenzoic acids, and nitrobenzaldehydes when treated with sulphuric acid and potassium sulphate has been investigated; it is found that the nitrogen content of the ortho-derivatives can be correctly estimated in this manner, but that the results for the meta- and para-derivatives are much too low. The favourable action of the hydroxy- or alkoxo-group in the ortho-position to the nitro-group is further shown by the fact that the process gives exact results with 2-nitroresorcinol, 3-nitro-*p*-cresol, and *o*-nitrophenetole, but low results with *p*-nitrophenetole. A further series of experiments shows that the presence of *o*-nitrophenol or of *o*-nitrobenzoic acid has a favourable influence on the behaviour of the corresponding meta- and para-derivatives, and that this action cannot be ascribed solely to their content of phenol or benzoic acid. The possibility that condensation products of the *o*-nitro-compounds may be the active agents has led to an investigation of the behaviour of phthalic acid, phthalic anhydride, and phenolphthalein under like conditions, but the expected favourable action was not observed. The use of salicylic acid appears particularly advantageous in the case of meta-compounds. It is somewhat remarkable that the three isomeric nitrocinnamic acids yield accurate results.

A further series of determinations is recorded with 2:4-dinitrophenol, 2:4-dinitro- α -naphthol, 2:4-dinitrobenzoic acid, 2:4-dinitrotoluene, 3:5-dinitrobenzoic acid, 2:6-dinitrotoluene, and 2:4:6-trinitrophenol; the results are considerably too low in every case, although concordant among themselves. The facts, however, that the 2:4-dinitro-compounds give higher values than the corresponding 3:5- or 2:6-dinitro-derivatives, and that 2:4-dinitrophenol gives results almost identical with those obtained with 2:4-dinitrotoluene, are in accordance with the observations made with the mononitro-compounds.

H. W.

Grete's Volumetric Method (for Estimating Phosphoric Acid). R. W. TUINZING (*Landw. Versuchs.-stat.*, 1919, 94, 191—195. Compare A., 1916, ii, 490).—This method was found

to be trustworthy. Directions are given for the preparation of the ammonium molybdate-gelatin solution used, and for the recovery of ammonium molybdate from the residual solutions. W. P. S.

Behaviour of certain Organic Arsenic Compounds in Marsh's Test. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1919, **58**, 385—390).—The addition of platinum chloride to promote the evolution of hydrogen is inadvisable, even in the case of mineral arsenic, since it may fix part of the arsenic as platinum arsenide. In the case of cacodylic acid, platinum chloride in large excess combines to form a double compound, cacodylplatinochloride, which may remain undecomposed. An analogous compound is formed between platinum chloride and methylarsinic acid. Cacodylic acid, in Marsh's test, produces an orange-yellow deposit in addition to the ordinary black deposit. This probably consists of erythrarsine. By heating the hydrogen flask to about 335° in a bath of melted lead only the orange-yellow deposit is obtained. Methylarsinic acid and neosalvarsan under the same conditions also yield yellow deposits, but these may be distinguished from the cacodylic acid deposit by the fact that during the formation of the former the gas does not form dense, white fumes. The gas from the methylarsinic acid test gives a yellow precipitate with Bettendorf's reagent (stannous chloride solution saturated with hydrogen chloride), whilst the lemon-yellow ring from neosalvarsan is only formed at a high temperature, does not change to black, and is readily soluble in ammonia solution. Atoxyl and salvarsan yield only the ordinary black rings in the test. [See also *J. Soc. Chem. Ind.*, 1920, 42A.]
C. A. M.

Separations in the Arsenic Group. WILHELM STRECKER and ADOLF RIEDEMANN (*Ber.*, 1919, **52**, [B], 1935—1947).—The authors recommend the following modification of the distillation method for the estimation of arsenic. The arsenic solution is placed in a flask provided with a dropping funnel and connected through an efficient worm condenser with a vessel containing water; the flask is half filled with concentrated hydrochloric acid, potassium bromide (1.5 grams), and a few pieces of porous earthenware are added. The contents of the flask are heated to gentle boiling, and thionyl chloride (10 c.c.) is gradually run in at such a rate that the time of addition is half an hour. The distillate is diluted with water to 700—800 c.c., boiled under reflux in a brisk current of carbon dioxide until sulphur dioxide is completely expelled, and the sulphur has collected (this should be the case in half an hour at the most), and filtered. Arsenic is estimated in the filtrate as the trisulphide. Phosphorus trichloride (25 c.c.) may replace the thionyl chloride, in which case the subsequent boiling of the distillate is unnecessary; on the other hand, the presence of phosphorous acid in the residue often causes complications in subsequent estimations. The method gives accurate results, and can be applied to the separation of arsenic from antimony, tin, copper, lead, mercury,

and iron, and for the estimation of arsenic and iron in arsenide of iron.

The separation of antimony from tin can be effected by taking advantage of the fact that antimony chloride is volatile at 155° — 165° from solutions in which the tin can be rendered non-volatile by the presence of phosphoric acid; the tin can be volatilised subsequently at a somewhat higher temperature by taking advantage of the fact that the addition of hydrobromic acid destroys the restraining action of the phosphoric acid. The authors have attempted to shorten the time required for this separation by utilising the catalysing action of hydrobromic acid from the commencement, but the results are unsatisfactory, since tin distils over with the antimony, the catalysing influence of hydrogen bromide out-balancing the restraining effect of phosphoric acid. On the other hand, the use of hydrobromic acid is very advantageous in the separation of antimony or tin alone from other elements, and does not require the absence of nitric acid. Thus, in the separation of antimony and copper, the hydrochloric acid solution of the metals is added to concentrated sulphuric acid (6 c.c.) and phosphoric acid (D 1.78, 7 c.c.) contained in a distillation flask connected with a receiver containing hydrochloric acid. The contents of the flask are heated at 160° , and a mixture of concentrated hydrochloric acid (10 volumes) and hydrobromic acid (D 1.78, 1 volume) is added at such a rate that the temperature remains constant. The antimony is completely removed in thirty minutes. The separation of antimony from lead is accomplished similarly.

Tin is quantitatively separated from copper and lead in an analogous manner; the solution of the metals in concentrated hydrochloric acid is treated with sulphuric acid (12 c.c.) and distilled at 160° with the regulated addition of the hydrochloric-hydrobromic acid mixture (20 c.c.). The process is complete in half an hour; the tin is precipitated from the distillate as the sulphide and weighed as the oxide. The method can be applied to the estimation of tin in brass.

The separation of antimony and tin from mercury cannot be effected in this manner, since the latter is also partly volatilised.

A novel type of filter tube is described which is constructed by drawing out the end of a piece of wide glass tubing so as to form a stem; a filter disc covered with asbestos rests on the shoulder of the wider tube, which is further provided with a ground-in cap in which a capillary opening is made. H. W.

Early Developments in Organic Macro- and Micro-analysis.

J. V. DUBSKÝ (*Chem. Weekblad*, 1919, **16**, 1482—1493).—The author gives a retrospect of the work of various experimenters in connexion with the analysis of organic substances, and indicates the lines along which research progressed. W. J. W.

Gas Analytical Combustion with Copper Oxide. E. OTT

(*J. Gasbeleucht.*, 1919, **62**, 89—90; from *Chem. Zentr.*, 1919, iv, 171—172).—Uncertainties in fractional combustion with copper

oxide arise in consequence of the dissociation, $\text{CuO} = \text{Cu} + \text{O}$, which can be eliminated by subsequent, repeated passage of the nitrogen over the material in the quartz tube, which is maintained at a low red heat. Preparation of chemically pure nitrogen by means of phosphorus and heated copper oxide is liable to error, and recourse should be had to the pyrogallol method. Copper oxide does not appear to be suitable for gas analyses in which the carbon dioxide formed by combustion is measured. H. W.

Estimation of Carbon Monoxide in Blood. D. D. VAN SLYKE and H. A. SALVESEN (*Proc. Soc. Exp. Biol. Med.*, 1919, **16**, 140; from *Physiol. Abstr.*, 1919, **4**, 374).—The blood is treated as in the estimation of oxygen by Van Slyke's method. A mixture of carbon monoxide and oxygen with a slight amount of nitrogen is obtained. The oxygen is absorbed by alkaline pyrogallol solution. The residual gas, after a correction has been made for nitrogen, is carbon monoxide. J. C. D.

A Micro-method for the Estimation of Calcium in Blood-serum, and other Organic Substances. D. J. DE WAARD (*Biochem. Zeitsch.*, 1919, **97**, 176—186).—The substances are evaporated and incinerated, and the salts of the ash extracted with dilute hydrochloric acid. The calcium is precipitated from the solution as the oxalate, which is centrifuged, washed, dissolved in dilute acid, and titrated with potassium permanganate. 0.1 Mg. of calcium can be estimated by this method with an error of 4%. S. S. Z.

A Direct Micro-estimation of Calcium in the Serum. D. J. DE WAARD (*Biochem. Zeitsch.*, 1919, **97**, 186—189).—All the calcium can be precipitated directly from the serum by means of ammonium oxalate and be estimated by the method described in the preceding abstract. The difference between an estimation carried out on the incinerated serum and on the original serum was only 0.001 mg. of calcium per c.c. S. S. Z.

Ferrous Sulphide as an Indicator in Acidimetry and a New Volumetric Method for the Estimation of Zinc. J. HOUBEN (*Ber.*, 1919, **52**, [B], 1613—1621).—Since the production of ferrous sulphide is prevented by the slightest traces of acids, it is possible to titrate an acid by adding a crystal of pure ferrous ammonium sulphate, passing in well-washed hydrogen sulphide (not enough to saturate the solution), and running in alkali until the black colour of ferrous sulphide is permanent. Experiments with hydrochloric and sulphuric acids on the one hand and alkali hydroxides and carbonates or borax on the other show that the end-point is quite as definite as it is in the case of methyl-orange or phenolphthalein. The only indistinct end-point is found when titrating sulphuric acid with borax, but here the difficulty may be overcome by running in more acid until the black colour just disappears again. The method is obviously useful in the case of coloured liquids, or when working in a bad light.

In the case of zinc salts, hydrogen sulphide completely precipitates zinc as sulphide from the sulphate if the solution is less than 0.2*N*, and from the chloride if the concentration is below 0.067*N*. A titration of the free acid produced would therefore be a means of estimating zinc in its neutral salts, and here the above use of a ferrous salt proves its worth. The solution is saturated with hydrogen sulphide, some ferrous ammonium sulphate is added, and alkali is run in, preferably borax solution, until the white turbidity becomes brown. A "back titration" with an acid is not possible in this case, however, without first filtering the zinc sulphide, as a double zinc-ferrous sulphide is formed which is not quickly broken up. Of course, cobalt and nickel salts must be absent.

Examples of the application of the method to metallic zinc, zinc salts, zinc ash, and blende show that the results approach those obtained by gravimetric analysis very closely, in fact much more so than those given by any other volumetric method. Blende is examined as follows. About 5 grams of the mineral are digested with 40 c.c. of concentrated hydrochloric acid and 40 c.c. of water, the solution filtered and saturated with hydrogen sulphide, filtered again, and diluted to 1000 c.c. with dilute hydrochloric acid. Portions of 50 c.c. are now neutralised with sodium carbonate, using methyl-orange, treated with hydrogen sulphide for half an hour, mixed with ferrous ammonium sulphate, and titrated with borax or sodium carbonate.

The alkalimetric titration of ferric salts may be carried out by employing the same principles.

J. C. W.

Electrometric Analysis with Potassium Ferrocyanide.

ERICH MÜLLER (*Zeitsch. angew. Chem.*, 1919, **32**, 351—352).—Electrometric titration of lead and zinc salts with potassium ferrocyanide solution is trustworthy, but the method fails in the case of other metals owing to the fact that the precipitates produced do not have definite compositions.

W. P. S.

Colorimetric Estimation of Lead Dioxide in Litharge.

WALLER V. MORGAN (*J. Ind. Eng. Chem.*, 1919, **11**, 1055).—The method depends on the fact that lead dioxide oxidises aniline to aniline-purple, and that the coloration obtained is proportional to the amount of the dioxide present. Five grams of the litharge containing lead dioxide are boiled for one minute with 2 grams of aniline hydrochloride dissolved in 10 c.c. of water and 5 c.c. of concentrated hydrochloric acid; the mixture is then filtered and the coloration exhibited by the filtrate compared with those given under the same conditions by litharge containing known amounts of lead peroxide.

W. P. S.

Complex Internal Salts in Quantitative Analysis. I.

I. BELLUCCI and A. CHIUCINI (*Gazzetta*, 1919, **49**, ii, 187—216).—The authors summarise and criticise published work on the applications of α -nitroso- β -naphthol and "cupferron" to the separation and estimation of metals.

For the separation of copper, neither of these reagents offers appreciable advantages over ordinary analytical methods, except perhaps for the separation of copper from arsenic and, more particularly, from antimony. For the separation of iron, cupferron is to be preferred to α -nitroso- β -naphthol, chiefly because the ferric precipitate obtained with the former withstands a greater degree of free mineral acidity, and is therefore more easily freed from extraneous metals, and also because the precipitate is less voluminous. α -Nitroso- β -naphthol serves principally as a reagent for cobalt, and also as a reagent for palladium, whilst cupferron acts as a reagent for titanium, zirconium, and vanadium, as well as for iron. The two compounds assume, indeed, the character of general reagents for groups of elements which contain, however, elements quite different from those usually classed together. T. H. P.

Detection of Cerium. FR. FEIGL (*Österr. Chem. Zeit.*, [ii], **22**, 124—126; from *Chem. Zentr.*, 1919, iv, 592).—Lecoq's reaction is much more distinctly obtained after the addition of a small quantity of an aluminium salt, but is not applicable in the presence of iron. A vivid blue coloration is obtained when cerium dioxide is moistened with a solution of benzidine in acetic acid; other cerous and ceric compounds, with the exception of cerous fluoride, cerous carbonate, and double sulphates of cerium, behave similarly. The reaction is most sensitive when the solution under investigation is made just alkaline with sodium or potassium hydroxide, heated to boiling, filtered, and the filter paper treated with a drop of benzidine solution; 0.02 mg. of cerium per litre can be thus detected. The other metals which belong to the ammonium sulphide group of the rare earths, with the exception of thallium, do not show the reaction. The absence of other oxidising agents and of manganese, cobalt, thallium, and chromate is essential, since the reaction depends on oxidation. Faintly acid solutions of iron also give the reaction; after previous addition of sodium or potassium hydroxide, a coloration is not observed. In the presence of iron, it is advisable to precipitate cerium as the fluoride and to convert the latter by alkali hydroxide into the hydroxide, since precipitated ferric hydroxide carries down notable amounts of cerium, which are thus removed from the sphere of action. H. W.

Soil Analysis. F. MÜNTER (*Landw. Versuchs.-stat.*, 1919, **94**, 181—189).—For the estimation of iron, aluminium, calcium, magnesium, potassium, and phosphoric acid in a soil, it is recommended that 300 grams of the sample be mixed with 900 c.c. of concentrated hydrochloric acid and shaken occasionally during forty-eight hours; the solution is then decanted, filtered, and 300 c.c. of the filtrate are evaporated with the addition of ammonium chloride. The residue obtained is treated with nitric and hydrochloric acids, again evaporated, this operation is repeated, and the final solution in hydrochloric acid is used, after separation of the silica, for the estimation of the above-mentioned constituents. W. P. S.

Application of Hæmatoxylin to the Detection of Iron in Tissues. J. MAWAS (*Compt. rend. Soc. Biol.*, 1919, **82**, 155—158; from *Chem. Zentr.*, 1919, iv, 245).—The author considers that the reaction of hæmatoxylin with ferrous ions is to be ascribed to salt formation, and not, as Macallum assumed, to oxidation. The latter's statement that the reaction only occurs with inorganic iron is incorrect, since iron compounds of the albumins, which are not acted on by hydrogen sulphide or ammonium sulphide, but are affected by potassium ferro- or ferri-cyanide, also show this change. The formation of Prussian-blue is a more delicate test for the presence of iron in tissues; nevertheless, the author has obtained useful results with hæmatoxylin, particularly in certain cases of disease of the eye. The affinity of the hæmatoxylin for the chromatin of the nucleus, whereby a similar coloration is developed, is disadvantageous.

H. W.

Brazilin and its Iron Lakes. J. MAWAS (*Compt. rend. Soc. Biol.*, 1919, **82**, 158—159; from *Chem. Zentr.*, 1919, iv, 245).—Brazilin is a more sensitive and more rapid reagent than hæmatoxylin (preceding abstract); its aqueous solution, pale red with an orange fluorescence, gives dark brown, insoluble lakes with ferrous salts. In aqueous or alcoholic solution, it colours tissue containing iron dark brown within a few minutes, whilst the nucleus becomes reddish-violet. Differentiation which may be necessary owing to over-colouring is effected with alcohol and chloroform, or, preferably, with alcohol containing 1% of hydrogen chloride. The nucleus becomes practically decolorised, whilst the iron pigment is unaffected; the former again becomes reddish-violet when washed with dilute aqueous alkali.

H. W.

Iodometric Estimation of Iron. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1565—1568).—The estimation of ferrous iron by means of iodine with addition of a pyrophosphate gives results which are about 3% too low owing to oxidation of the iodine by dissolved oxygen in the solutions. If sulphuric acid and sodium hydrogen carbonate are added to eliminate the oxygen, the error is reduced to 0.8—1%. A more suitable method which gives accurate results is the following: 25 c.c. of 0.1N-potassium bromate and 10 c.c. of 25% phosphoric acid are added to 10 c.c. of 0.1N-ferrous solution to which a few drops of acid have been added. After remaining for five minutes in a stoppered flask, 5 c.c. of potassium iodide and 2 drops of molybdate solution are added, the iodine being titrated after five minutes with thiosulphate.

The purpose of the phosphoric acid is to combine with the ferric ions and prevent them interacting with the potassium iodide, and the molybdate is added to accelerate the reaction of the bromate and iodide.

W. J. W.

Volumetric Estimation of Iron. J. HOUBEN (*Ber.*, 1919, **52**, [B], 2072—2076. Compare this vol., ii, 53).—The process

permits the estimation of ferrous and ferric iron and free mineral acid in a solution.

A portion of the solution is completely reduced by hydrogen sulphide and titrated with *N*-potassium or sodium hydroxide solution until the dark coloration due to the incipient precipitation of ferrous sulphide is observed, which does not disappear after vigorous shaking; the free acid plus one-third of the acid originally combined with the ferric salt is thereby estimated. A second portion of the solution is reduced with sulphur dioxide (air being completely excluded), most of the excess of the latter is removed by boiling, and the cooled solution is titrated with *N*-alkali as before, after being treated with hydrogen sulphide, which completes the removal of sulphur dioxide. The free acid plus two-thirds of the acid originally united to the ferric iron is thus estimated. The difference between the two titrations multiplied by three gives the number of c.c. of *N*-ferric chloride solution originally present. If this number is subtracted from the smaller of the two burette readings, the difference is the number of c.c. of *N*-acid which were uncombined in the solution. The ferrous salt is estimated in the usual manner. Test analyses show the method to have a high degree of accuracy.

H. W.

Separation of Iron, Aluminium, Chromium, Glucinum, Titanium, and Zirconium by the Sodium Carbonate Method.

P. WENGER and J. WUHRMANN (*Ann. Chim. anal.*, 1919, [ii], 1, 337—339).—A method described previously by Wenger and Wunder (A., 1912, ii, 687) may be applied when the mixture contains titanium or zirconium, but not both. After fusion with sodium carbonate, the insoluble iron and zirconium oxides may be treated with hydrochloric acid (1:1), in which the zirconium oxide is insoluble. In the absence of zirconium, iron and titanium may be separated by one of the known methods, even in the presence of glucinum. [See, further, *J. Soc. Chem. Ind.*, 1920, 46A.]

W. P. S.

A New Method for the Volumetric Estimation of Nickel.

JOSEF HOLLUTA (*Monatsh.*, 1919, 40, 281—291).—The process depends on the fact that, when a nickel salt reacts with dimethylglyoxime, acid is liberated, which is estimated by titration with alkali in the presence of phenolphthalein or methyl-red.

The standard *N*/50-solution is prepared by dissolving 4.6400 grams of pure dimethylglyoxime in the requisite quantity of 97% alcohol (300—400 c.c.); 20 c.c. of *N*-potassium hydroxide solution are added with constant shaking, and the solution is diluted to 1000 c.c. with distilled water free from carbon dioxide and filtered after twenty-four hours from any slight precipitate of potassium carbonate. (The alcohol used must be free from aldehyde and neutral in reaction.) The alkali content of the solution is checked by titration with standard acid, using phenolphthalein or methyl-red as indicator. The nickel solution under examination is diluted

to the required extent, and exactly neutralised with $N/10$ - or $N/50$ -potassium hydroxide solution. 2—5 C.c. of the standard solution are added, and, after vigorous agitation, the solution is gently warmed, whereby the precipitate is caused to collect, leaving a clear liquor; the standard solution is then gradually added with frequent agitation until the solution acquires a permanent, pale pink coloration. In consequence of the bulky nature of the nickel precipitate, the amount of the metal in the solution should not exceed 0.03 gram.

The method is particularly advantageous in dealing with very small quantities of nickel, and titration can readily be effected with $N/100$ -solutions if methyl-red is substituted for phenolphthalein as indicator. The results are not affected by the presence of the alkali salts of strong acids. Further details are promised in a subsequent communication.

H. W.

Iodometric Estimation of the Chromic Acid in Lead Chromate. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1919, **108**, 267—272).—The iodometric method of estimating chromic acid has not hitherto been used for lead chromate on account of the impossibility of completely decomposing the chromate by means of dilute sulphuric acid. Dilute hydrochloric acid dissolves lead chromate completely, but hydrochloric acid has a reducing action on chromic acid, with liberation of free chlorine, and has therefore not been used to dissolve lead chromate. It is now found, however, that if the hydrochloric acid is sufficiently dilute, its reducing action is negligible. Experiments showed that when acid of 1.25*N* strength or less was used, in the proportion of 25HCl to 1 mol. of chromate, no reduction took place after boiling the solution for three hours. With stronger hydrochloric acid, the rate of reduction increased rapidly with the concentration of the acid. For carrying out an analysis, about 0.3 gram of lead chromate is dissolved in 50 c.c. of 1.25*N*-hydrochloric acid by gently heating. The solution is cooled, 1 gram of potassium iodide added, allowed to remain for ten minutes, diluted with 100 c.c. of water, and the free iodine titrated with sodium thiosulphate. There is no need to filter off the precipitated lead iodide, as the colour of this does not interfere with the end-point. After the end of the titration, free iodine again appears after a short time. This is due to atmospheric oxidation of hydriodic acid, a reaction which appears to be catalysed by the lead iodide present. The results obtained by this method are generally about 0.5% too high.

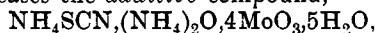
E. H. R.

Detection of Molybdenum by means of Xanthic Acid. J. KOPPEL (*Chem. Zeit.*, 1919, **43**, 777—778).—Molybdenum compounds give a characteristic red to plum-coloured reaction with xanthic acid, which was first described by Siewert (*Zeitsch. ges. Naturw.*, 1864, **23**, 5). The test is preferably applied by acidifying the solution with a mineral acid, after the addition of a trace of solid potassium xanthate, and is capable of detecting molybdenum in a solution containing 0.00000064 gram per c.c. The reaction is

weaker when phosphoric, formic, or acetic acid is used for the acidification, and much weaker with salicylic acid, whilst when oxalic, citric, or tartaric acid is used, there is little, if any, coloration. Analogous xanthic compounds are formed by copper, iron, cobalt, nickel, etc., but the colorations do not interfere with the molybdenum test. Vanadic acid forms a yellow compound and uranic acid a brown compound, which, like the molybdenum compound, are soluble in ether and other organic solvents. Tungstic acid, if present in very large preponderance, may interfere with the test. The molybdenum compound may be obtained as a black oil by mixing a solution of 2 grams of ammonium paramolybdate with 1 gram of potassium xanthate. When vigorously stirred, this oil solidifies, forming black crystals with green surface reflections. The mean analyses of Siewert's solid preparation agree with the formula $\text{MoO}_3(\text{OEt}\cdot\text{C}\cdot\text{S}\cdot\text{S}\cdot\text{H})_2$. [See also *J. Soc. Chem. Ind.*, 1920, January.]
C. A. M.

Colour Reactions of Molybdenum and Tungsten. II.

G. A. BARBIERI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 390—392. Compare A., 1919, i, 549).—According to Péchard (A., 1894, ii, 319), replacement of the hydrochloric or sulphuric acid used in Braun's reaction by acetic acid results in the formation of a yellow coloration, and, with concentrated solutions, of a yellow, crystalline precipitate, due to conversion of the molybdate into trimolybdate, and union of this with the thiocyanate present to form an additive compound, for instance, $\text{KCNS}\cdot\text{K}_2\text{O}\cdot 3\text{MoO}_3\cdot 4\text{H}_2\text{O}$. On repetition of Péchard's reaction with ammonium thiocyanate and ammonium permolybdate or tri- or tetra- or normal molybdate, the author finds that in all cases the *additive* compound,



is formed, and in no case an additive compound of the trimolybdate. From potassium trimolybdate and thiocyanate in presence of acetic acid, the corresponding *compound*, $\text{KSCN}\cdot\text{K}_2\text{O}\cdot 4\text{MoO}_3\cdot 5\text{H}_2\text{O}$, is formed; both potassium and ammonium compounds form yellow, acicular crystals.

Ammonium tetramolybdate, $(\text{NH}_4)_2\text{O}\cdot 4\text{MoO}_3\cdot 2\frac{1}{2}\text{H}_2\text{O}$, may be obtained by the action of acetic acid on ammonium permolybdate in aqueous solution (compare Junius, A., 1905, ii, 825).

T. H. P.

Qualitative and Quantitative Test for Molybdenum in Steel and Iron. SIEGFRIED LAURENS MALOWAN (*Zeitsch. anorg. Chem.*, 1919, 108, 73—80).—A specific and very sensitive test for molybdenum is given by xanthic acid. The test is best carried out with freshly prepared xanthate solution in the following manner. Absolute alcoholic potash is shaken with excess of carbon disulphide until no more of the latter is dissolved. To the solution so obtained, 30% acetic acid is added until it shows a slight yellow turbidity, and the reagent is added drop by drop to the solution to be tested. If molybdenum is present, an intense red colour

develops, which is quite stable in water, and the intensity of which is proportional to the quantity of molybdenum present. The sensitiveness of the reaction is such that 0.000005 gram of molybdenum in 0.0007% solution can be detected with certainty in presence of other elements. The coloured product is readily soluble in ethyl or amyl alcohol, ether, or chloroform, less easily in petroleum and benzene. It is readily extracted from its reddish-violet ethereal solution by alkalis, from which acids precipitate it. The ethereal solution decomposes on keeping, with formation of molybdenum sulphide. The reaction is not given by vanadium, tungsten, titanium, or uranium; chromates give a dark coloration with xanthic acid, and should be reduced, if present, before the test is made. The reaction can be used for the colorimetric estimation of molybdenum, the coloured product being extracted with a mixture of 65% ether and 35% light petroleum, and a mixture of 30% ether and 70% light petroleum used for dilution for comparison with the standard solution. If pure ether is used, decomposition takes place too rapidly for accurate determinations to be made. E. H. R.

Colorimetric Method for the Estimation of Small Quantities of Uranium. MÜLLER (*Chem. Zeit.*, 1919, **43**, 739—740).—The method depends on the red coloration obtained when a uranyl salt is treated with sodium salicylate; the coloration yielded by any uranyl salt solution is compared with that produced by a known amount of uranium under the same conditions. Free mineral acid, acetic acid, iron, alcohol, or acetone must not be present, but neutral alkali salts do not interfere. The method is suitable for the estimation of uranium in solutions containing as little as 0.02% of the metal. W. P. S.

Estimation of Zirconium by the Phosphate Method.

G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1919, **41**, 1801—1808).—Zirconium can be quantitatively precipitated as secondary zirconium phosphate in cold or tepid solutions containing from 2% to 20% by weight of sulphuric acid, provided that a ten- to one hundred-fold excess of the precipitant, diammonium hydrogen phosphate, is used. Hydrolysis, which occurs when the phosphate precipitate is washed with water, can be almost entirely avoided by the use of a cold 5% ammonium nitrate solution for washing. Zirconium pyrophosphate, for which the ZrO_2 factor is 0.4632, is obtained on ignition of a secondary zirconium phosphate which has been washed with ammonium nitrate solution. No definite composition can be ascribed to the compound resulting when secondary zirconium phosphate which has been washed with water is ignited. Zirconium can be quantitatively separated as phosphate in a 20% sulphuric acid solution from iron, aluminium, chromium, cerium, and thorium. The separation from titanium can also be effected provided hydrogen peroxide is present. J. F. S.

Gas-analytical Separation of Acetylene, Ethylene, and Benzene. W. D. TREADWELL and F. A. TAUBER (*Helv. Chim. Acta*, 1919, **2**, 601—607).—The quantitative absorption of acetylene from mixtures containing it, together with ethylene and benzene vapour, is conveniently effected with a solution of mercuric cyanide (20 grams) in 2*N*-sodium hydroxide solution (100 c.c.); the gas is shaken with the mixture (5 c.c.) for one to two minutes, at the end of which the acetylene is completely absorbed, whilst ethylene and benzene vapour are unaffected.

A solution of mercuric nitrate (20 grams) in 2*N*-nitric acid (100 c.c.) which has been saturated with sodium nitrate is recommended for the absorption of ethylene in the presence of benzene vapour; the gas is shaken with 5—10 c.c. of the solution for two to three minutes. Propylene appears to behave similarly to ethylene, since it is indifferent to alkaline mercuric cyanide solution, whilst readily absorbed by mercuric nitrate solution.

H. W.

Dehydrogenation of Hydrocarbons by means of Palladium-black. JENŐ TAUSZ and NIKOLAUS VON PUTNOKY (*Ber.*, 1919, **52**, [B], 1573—1583).—Zelinski has shown that *cyclohexanes* are converted into benzene hydrocarbons by exposing them to the action of palladium-black at 300°, whereas hexane and *cyclopentanes* are unchanged (*A.*, 1913, i, 167). This seemed to offer a process whereby *cyclohexanes* could be estimated in the presence of paraffins, and a method has now been developed which gives satisfactory results within certain limits.

The first difficulty to be overcome was the preparation of a sufficiently active catalyst, for Zelinski's agent is spoilt by mixtures of paraffins and *cyclohexane* long before the latter is completely dehydrogenated. In the reduction of palladium solutions, it is usual to employ formic acid, any excess being destroyed by the palladium-black itself. It seemed possible, therefore, that the activity of the catalyst would suffer in such a treatment, and as it was found, that the activity towards formic acid is parallel to the activity towards *cyclohexane*, it was decided to use no more than the theoretical quantity of the reducing agent. This has the desired effect, the catalyst being much more active. For example, two specimens of 1 gram each, prepared by Zelinski's method, produced 1·8 and 11·2 c.c. of gas from formic acid, but ten samples made by the new process, which is described in detail, gave on an average 458 c.c., one portion developing as much as 840 c.c.

With such an active catalyst, the quantitative dehydrogenation of *cyclohexane* in various mixtures with hexane may be easily realised; but then another disturbing factor appears, namely, that at 300° the saturated paraffins themselves are to a certain extent converted into unsaturated hydrocarbons by palladium black. The small amount of hydrogen set free by the paraffins, however, reaches a constant volume after an hour or two, and although a little more gas is liberated when the catalyst is renewed, an equilibrium

is soon established. A similar equilibrium is reached when the olefines are heated with an excess of hydrogen, that is, the hydrogenation is never quite complete. The volume of hydrogen produced by the paraffins is relatively small compared with the yield from the *cyclohexanes*, so, within certain limits, the proportion of the latter hydrocarbons in a mixture can be gauged from the amount of hydrogen liberated. The limit is generally about 1% of cyclic hydrocarbon, but in some experiments it was as low as 0.5%. For mixtures containing less than this, only the chemical proof of the presence of benzene will suffice. The reaction with trioxymethylene and sulphuric acid is recommended.

For quantitative purposes, a special apparatus is described. The catalyst (12 grams) is contained in a tube heated in a simple electric furnace, and the vapour is continually circulated. The volume of oil employed varies from 10 c.c. for rich mixtures to 100 c.c. In the experiments described, the following volumes of hydrogen were produced by 1 c.c. of hydrocarbon at 300° (or 270° in the case of the methyl derivatives): *cyclohexane*, 614 c.c.; *methylcyclohexane*, 618 c.c.; 1:3-dimethyl*cyclohexane*, 504 c.c.; *isopentane*, 38 c.c.; *n-hexane*, 40.8 c.c. (after renewing the catalyst five times); *n-heptane*, 32.5 c.c.; *n-octane*, 36 c.c.

As an important application of the method, the analysis of a sample of hexane, b. p. 69—71°, from American petroleum is recorded. Whereas 30 c.c. of synthetic *n-hexane* gave only 338 c.c. of hydrogen, 30 c.c. of the natural oil yielded 446 c.c. under exactly the same conditions. This corresponds with 2.4% of *cyclohexane* in the sample, and actually 0.5592 gram of pure dinitrobenzene was obtained from the dehydrogenated 30 c.c. of oil.

J. C. W.

Criteria of the Degree of Purity of Commercial Toluene.

JOHN SCOTT LUMSDEN (T., 1919, 115, 1366—1372).

Differentiation of Methyl and Ethyl Alcohols. PANNWITZ (*Pharm. Zentr.-h.*, 1919, 60, 441—442).—Although crystallised copper sulphate is insoluble in ethyl alcohol and dissolves in methyl alcohol to give a blue solution, this test is useless for distinguishing methyl alcohol from ethyl alcohol, owing to the fact that a small quantity of water destroys the blue colour of the methyl alcohol solution. The quantity of added water must be increased to 35% by vol. before the blue colour reappears, and at this dilution ethyl alcohol also begins to dissolve copper sulphate. The same effects are noticed when ferrous sulphate is used in place of copper sulphate. The borax flame test for methyl alcohol also fails when water is present.

W. P. S.

Influence of the Presence of Trimethylene Glycol on the Estimation of Glycerol by the Zeisel *iso*Propyl Iodide Method. C. A. ROJAHN (*Ber.*, 1919, 52, [B], 1454—1460).—Although trimethylene glycol produces no silver iodide precipitate when

digested by itself in the Zeisel apparatus at 120—125°, it does so behave when added to glycerol. In fact, the excess of silver iodide corresponds with the amount of *s*-di-iodopropane produced if the quantity of trimethylene glycol is small. As a consequence, Zeisel's method is not applicable to the estimation of fermentation glycerol (the German "protol"-glycerol), for this contains trimethylene glycol.

J. C. W.

Chromatic Reactions of Formaldehyde with certain Aromatic Compounds. ARTURO ROSSI (*Boll. Chim. Farm.*, 1919, **58**, 265—270).—Colorations, which are not necessarily distinctive of the aldehyde, are given by formaldehyde in 0.1 or 0.001% aqueous solution, when added to sulphuric acid containing a trace of certain aromatic compounds in solution. Applied as a zone reaction, the following colorations are obtained: *Gallic acid*, a reddish-brown ring, and, on shaking the tube, a green liquid changing to greyish-green. *Tannic acid*, a reddish-brown ring, and a liquid bluish-green at the bottom, but subsequently brownish-red throughout. *Pyrogallol*, a light rose-coloured ring, and liquid. The test is capable of detecting 0.00001% of formaldehyde. *Salicylic acid*, a light rose-coloured ring and solution. *Catechol* and *resorcinol*, various red rings and liquids. *β -Naphthol*, a violet-red ring, and brownish-black liquid with green fluorescence. *Benzonaphthol*, similar colour reactions. *Phenyl salicylate*, carmine-red ring and reddish-yellow liquid, becoming pink on dilution. *Phenolphthalein*, no ring, but an orange liquid changing to carmine-red on shaking. Dilution with water causes a carmine-red precipitate to separate.

C. A. M.

Estimation of Formaldehyde in Blood. E. SALKOWSKI (*Biochem. Zeitsch.*, 1919, **97**, 129—135).—The protein of the blood is hydrolysed with gastric juice. The hydrolysed mixture is distilled and *N*/10-iodine added to the distillate. The residual iodine is then titrated with thiosulphate. The formaldehyde found amounted to only 85.73% of the quantity added to the blood.

S. S. Z.

Estimation of Acetone and Acetoacetic Acid with Autenrieth's Colorimeter. H. SCHALL (*Münch. med. Woch.*, 1919, **66**, 812—814; from *Chem. Zentr.*, 1919, iv, 562).—Description of the application of Autenrieth's colorimeter to the colorimetric estimation of acetone according to Legal and to the estimation of acetoacetic acid. Gerhardt's iron chloride reaction is suitable for the estimation of considerable concentrations of the latter (above 0.5%), whilst, at greater dilutions, Rimini's ethylenediamine test is used. The former has the advantage of easy manipulation and constancy of colour, whilst the latter is more sensitive and gives a pure tint which, however, rapidly loses in intensity. Empirical solutions of dyes are used as standards. When acetone and acetoacetic acid are present simultaneously, the estimation of acetone requires

the correction of a factor, since acetoacetic acid gives a positive Legal's reaction which is 5.55 as intense as that of acetone.

H. W.

An Acetoneurometer. A. ADLER (*Münch. med. Woch.*, 1919, **66**, 722—723; from *Chem. Zentr.*, 1919, iv, 398).—A colorimetric method of estimating acetone is described which is based on Legal's test. A mixture of urine (10 c.c.), sodium hydroxide solution (20%, 1 c.c.), and sodium nitroprusside solution (33%, 0.5 c.c.) is well shaken, and acetic acid (20 drops) is added. The colour is compared with that given by mixing Neutral-red, New-blue, and Diamond-phosphine. Solutions of the dyes of the following concentrations are prepared: Neutral-red, 1:1000; New-blue, 1:1000; Diamond-phosphine D, 1:100. Ten c.c. of the first, 3 c.c. of the second, and 0.6 c.c. of the third solution are mixed with water, 5 c.c. (solution I), and correspond with 0.1% of acetone. Ten c.c. of solution I diluted with an equal volume of water correspond with 0.08% of acetone; 5 c.c. of solution I with 10 c.c. of water are equivalent in colour to 0.05% of acetone; 5 c.c. of solution I with 15 c.c. of water correspond with 0.01% of acetone. Five c.c. of a solution of neutral-red (10 c.c.), new-blue (1 c.c.), and diamond-phosphine (0.1 c.c.) with water (50 c.c.) correspond with 0.005% of acetone. The solutions are placed in tubes similar to those used in the experiment, which are subsequently sealed. The five standards are in practice sufficient for ascertaining the acetone content of a urine. H. W.

Methylene-blue as a Reagent for the Detection of Sugar in Urine. F. URZ (*Süddeut. Apoth. Zeit.*, 1919, **59**, 280—281; from *Chem. Zentr.*, 1919, iv, 212—213).—According to the author's observations, urines which contain sugar always give a positive reaction with solutions of methylene-blue, even when Lieber's modification of the test is used. Aqueous solutions of dextrose behave similarly, but sucrose, carbamide, uric acid, and saliva do not give the reaction. Milk behaves similarly to urine containing sugar. Whilst aqueous solutions of hexamethylenetetramine do not react with methylene-blue, the urines of patients to whom the drug has been administered behave similarly to saccharine urines, but do not give a positive result with Fehling's solution or Nylander's reagent. Normal urines, free from sugar, also give a positive reaction with methylene-blue when they have been preserved for some days and are partly decomposed, and this is particularly noticeable if they have been rendered alkaline with potassium hydroxide. Artificial gastric juice and glycuronic acid are also able to decolorise methylene-blue. The substance, therefore, is not a suitable reagent for the detection of sugar in urine.

H. W.

Rapid Method for the Estimation of Sugar in Urine. OTTO MAYER (*Arch. Hyg.*, 1919, **88**, 184—197; from *Chem. Zentr.*, 1919, iv, 211—212).—The detection of sugar in urine is best carried out by Trommer's test, for the performance of which, as also for Fehling's and Nylander's reactions, practical directions are given.

The estimation of sugar is effected in the following manner: urine (10 c.c.) is placed in a 100 c.c. stoppered measuring cylinder, sodium hydroxide (15%, 10 c.c.) is added, and the solution is diluted to 50 c.c. with water; copper sulphate solution (25 grams per litre) is gradually added with gentle shaking until the precipitate, which denotes the end of the reaction, practically completely redissolves on vigorous agitation, leaving only a just perceptible but permanent turbidity, which slightly increases in course of time. Under these conditions each c.c. of copper sulphate solution corresponds with 0.1% of dextrose. If the urine contains more than 4% of sugar it is preferable to take only 5 c.c., whilst if the content is 0.5—1% 20 c.c. may be measured out. Separation of alkaline earth phosphates from urines which have been treated with alkali and diluted from 2.5 to 10 times occurs only when these are present in exceptional quantity. In this case, since the sensitiveness of the end-point may be greatly reduced, it is advisable to treat 20 c.c. of the urine with 20 c.c. of sodium hydroxide solution, to filter the solution after dilution to 100 c.c., and to perform the titration with 50 c.c. of the clear filtrate.

For the detection of acetone, powdered sodium nitroprusside (0.05—0.1 gram) is shaken with about 10 c.c. of urine, about 1 c.c. of sodium hydroxide (15%) is added to the solution, which is then acidified with acetic acid (30%, 2 c.c.). In this form the test is so sensitive that distillation is only necessary with such urines as are deeply coloured or contain only small amounts of acetone. The most suitable reagent for the detection of acetoacetic acid is a mixture of liquor ferri. sesquichl. (5 c.c.) and sodium chloride solution (1:3, 95 c.c.), the reaction being performed as a ring test. H. W.

Volumetric Estimation of Sugar in Milk. J. L. MAYER (*J. Amer. Pharm. Assoc.*, 1919, **8**, 551—553).—Benedict's method for the estimation of dextrose in urine as modified by the author was applied to the estimation of lactose in milk. The results were trustworthy. CHEMICAL ABSTRACTS.

[Estimation of Invert-sugar by Fehling's Solution.] J. D. VAN LEEUWEN (*Chem. Weekblad*, 1919, **16**, 1425—1426).—In the titration of invert sugar solution with Fehling's solution, dilution of the latter with four times its volume of magnesium sulphate solution (0.5 gram per litre) causes the precipitated cuprous oxide to settle rapidly, and thus gives a clear solution for testing with potassium ferrocyanide and acetic acid; the solution must be cooled for this test. W. J. W.

Estimation of Carbamide by means of Sodium Hypobromite. E. DEKEUWER and L. LESCOEUR (*Compt. rend. Soc. Biol.*, 1919, **82**, 445—447; from *Chem. Zentr.*, 1919, iv, 350).—In the estimation of pure carbamide by bromine and alkali hydroxide, a slight deficit is always observed which has about the same magnitude when calculated from the nitrogen evolved or from the bromine used; the error is doubled when the calculation is based on the

amount of carbon dioxide formed. The course of the reaction appears to depend on the relative quantities of alkali and carbamide. A factor can be applied based on the results obtained. In the estimation of carbamide in urine, high results are obtained when the calculation is based on the bromine which is utilised (particularly in the case of urines containing sugar), since bromine is also used in the oxidation of substances other than carbamide. The results deduced from the amounts of nitrogen and carbon dioxide formed respectively generally agree well among themselves; in the case of urines containing sugar, the values calculated from carbon dioxide are lower than those reckoned from nitrogen.

H. W.

Estimation of Carbamide in Blood and Urine. C. BRAHM (*Deut. med. Woch.*, 1919, **45**, 803; from *Chem. Zentr.*, 1919, iv, 442).—A criticism of Citron's method of estimating carbamide. The latter is not quantitatively decomposed by sodium hypobromite according to the scheme: $\text{CO}(\text{NH}_2)_2 + 3\text{NaBrO} = 13\text{NaBr} + \text{CO}_2 + 2\text{H}_2\text{O} + \text{N}_2$, since a proportion of the nitrogen is retained as nitric acid or cyanuric acid. In the author's opinion all methods which are based on the reaction between carbamide and sodium hypobromite are to be rejected. The form of apparatus proposed is also open to many objections.

H. W.

Estimation of Carbamide in Urine by means of Urease. ARNOLD HAHN (*Deut. med. Woch.*, 1919, **45**, 911—912); from *Chem. Zentr.*, 1919, iv, 562—563).—The author's method has been modified by Horváth and Kadletz by the introduction of a receiver containing acid; the alteration is regarded as adding an unnecessary complication to the process.

H. W.

Detection of Hydrocyanic Acid in a Case of Poisoning. Its Post-mortem Transformation into Sulphocyanic Acid. L. CHELLE (*Compt. rend.*, 1919, **169**, 852—854. Compare A., 1919, ii, 529, 530).—A dog was poisoned by administering potassium cyanide and an autopsy immediately performed, the various organs being divided up and kept in stoppered sterile flasks for various lengths of time. Using the methods previously described (*loc. cit.*), hydrocyanic acid as such, but no thiocyanic acid, was detected after two hours in the brain, lungs, and blood, but not in the liver. After eight days no hydrocyanic acid as such could be detected in any of the organs or the blood, but thiocyanic acid was found in the blood, lungs, and brain, but not in the liver. Further, the amount of thiocyanic acid found in the lungs and brain, but not in the blood, corresponded with far more than the amount of hydrocyanic acid found at the end of two hours. This is explained on the grounds that a certain amount of hydrocyanic acid becomes enclosed in the cells in the first few hours after death and is not set free by the methods of estimation used, but after eight days, as a result of

putrefaction and consequent cytolysis, it is all liberated by the reagents and thus estimated. W. G.

Estimation of Ferricyanide and Ferrocyanide. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1618—1626).—The author has investigated the iodometric estimation of potassium ferricyanide. The acidity of the solution has an appreciable influence on the reaction; if the concentration is sufficiently high, accurate results are obtained after allowing the solutions to remain for only half a minute. Rupp's method for the estimation of ferrocyanide is inaccurate. An outline is given of the theoretical interpretation of the iodometric estimation of ferri- and ferro-cyanide. The reducing action of ferrocyanide is increased by rise of temperature.

W. J. W.

Proteinogenous Amines. II. A Micro-chemical Colorimetric Method for Estimating Iminazole Derivatives.

KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 497—519).—The method depends on the colour reaction between compounds containing the iminazole ring and sodium *p*-diazobenzenesulphonate. It can be applied directly to practically any iminazole derivative, gives equally good results whether applied to pure solutions or mixtures, and is capable of estimating with a fair degree of accuracy as little as 0.00001 gram of any of the iminazoles. The iminazole derivative is added under certain conditions to a mixture of sodium carbonate and the *p*-diazobenzenesulphonic acid in one cup of a Duboscq colorimeter, and the height of liquid in this cup is set at 20 mm. The other cup is filled with an appropriate indicator solution, and the height varied until the colours match. From tables which have been prepared, the amount of the iminazole derivative can be read off. Certain substances interfere with the method, notably ketones, alcohols, ammonium salts, and proteins. Animal charcoal must not be used to decolorise solutions which it is desired to test for iminazole derivatives, as loss by adsorption occurs. J. C. D.

Proteinogenous Amines. III. A Quantitative Method for Separating Histamine from Histidine.

KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 521—538).—The colorimetric process described in the preceding abstract may be utilised for estimating certain components of mixtures of iminazole derivatives. A mixture of these derivatives, such, for example, as that which is formed by the action of bacteria on histidine in the presence of salts and dextrose, is treated with sufficient sodium hydroxide to make the whole a 20% solution of alkali. This solution is extracted repeatedly with amyl alcohol, whereby the histamine, ammonia, methyliminazole, and other amines are removed. This extract is termed the histamine fraction, whilst the residual liquid containing histidine, iminazole, propionic, acetic and lactic acids is called the histidine fraction. The amount of histidine can be determined by an estimation of the

amino-nitrogen in the second fraction. A colorimetric estimation on the same fraction will indicate whether there are other iminazole derivatives present other than histidine.

The histamine and methyliminazole are extracted from the amyl alcohol by 1.0*N*-sulphuric acid, and a colorimetric estimation will give on this extract an indication of the total iminazole substances present. The methyliminazole may be estimated directly by the fact that it is volatile in steam. The colorimetric estimations on these two fractions will give by difference the amount of histamine present.

J. C. D.

Direct Estimation of Non-amino-nitrogen in the Products of Protein Hydrolysis. ALMA HILLER and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1919, **39**, 479—488).—An extension of the method of protein analysis introduced by Van Slyke (*A.*, 1915, ii, 851). The filtrate from the phosphotungstates of the diamino-acids, representing 2 or 3 grams of protein, is concentrated to 150 c.c. Portions of this solution are used for estimations of the total nitrogen and amino-nitrogen, as described in the original paper. Of the residue, 100 c.c. are measured into a separating funnel of 500 c.c. capacity, and are rendered free from phosphotungstic acid by extraction with amyl alcohol-ether mixture in the presence of hydrochloric acid. The solution is concentrated in a vacuum to about 50 c.c., and washed into a 100 c.c. volumetric flask. Of this solution, 20 c.c. portions are used for the non-amino-nitrogen estimation. Each portion is placed in a small Kjeldahl flask with 1.2 c.c. of 30% sodium nitrite and 5 c.c. of concentrated hydrochloric acid. When deamination is completed, the solution is neutralised to alizarin with 10% sodium hydroxide and reduced with zinc-copper couple. After making alkaline with magnesium oxide, the ammonia formed by the reduction is removed by boiling, and residual nitrogen is estimated by the Kjeldahl process. The results by this direct method agreed closely, in analyses of caseinogen and gelatin, with the results obtained indirectly by the original procedure.

J. C. D.

Apparatus for Rapid Gastric Analysis, together with a Method for the Preservation of Starch Solution. RAYMOND J. MILLER (*J. Ind. Eng. Chem.*, 1919, **11**, 963—964).—A convenient arrangement of burettes, indicator reservoirs and delivery tubes, an automatic pipette, etc., attached to one stand, and intended for the estimation of total acidity, free acidity, and amino-acid nitrogen (formaldehyde method) in gastric fluids. The starch solution is preserved under a layer of liquid "petrolatum," with or without the addition of a small quantity of toluene.

W. P. S.