ABSTRACTS OF CHEMICAL PAPERS.

## Analytical Chemistry.

Sources of Error in Alkalimetry. By P. Dobriner (Zeit. angw. Chem., 1895, 259—262).—The author states that if a sample of any acid is titrated with standard soda under exactly the same conditions as when doing the check experiment, no sources of error are introduced by the presence of a small quantity of carbonate in the alkali.

L. DE K

Luteol, a new Indicator. By WILHELM AUTENRIETH (Arch. Pharm., 1895, 233, 43—48).—See this vol., i, 572.

Modification of Soxhlet's Extraction Apparatus. By A. Philips (Ber., 1895, 28, 1475). The side tube of the ordinary Soxhlet, which conveys the vapour of the liquid to the condenser, is replaced by an annular space which surrounds the extraction space into which the liquid drops after condensation. This acts as a vapour jacket, and keeps the extracting liquid at a temperature near its boiling point throughout the extraction, a considerable amount of time being thus saved.

A. H.

Estimation of Halogens by Carius' Method: Application of Volhard's Modification. By Fritz W. Küster (Annalen, 1895, 285, 340—348).—The author describes in detail the conditions under which halogen determinations are carried out in the Marburg laboratory. By enveloping the tube in blotting paper, risk of explosion is minimised, and the temperature may be raised as rapidly as possible to  $320-340^{\circ}$ , at which most substances are completely decomposed after an exposure of two hours. On diluting the contents of the tube with water, it suffices, when chlorine is being estimated, to allow the liquid to remain for a short time on the water bath, but in the case of bromine and iodine more systematic treatment with boiling water is necessary; the silver haloid is then transferred to a Gooch crucible, which is dried for  $1\frac{1}{2}$  hour in the vapour of boiling xylene.

In Volhard's modification of Carius' method, a known quantity of silver nitrate is employed, and after removing the silver haloïd, the excess of silver is determined by titration with ammonium thiocyanate. The author, in applying this modification, has found it untrustworthy, titration invariably indicating the presence of silver in too small a quantity. Careful quantitative experiments have traced this discrepancy to the familiar brown stain acquired by tubes employed in halogen determinations, the coloration being due to silver, which is taken up by the glass in quantities which increase with the temperature and duration of heating.

M. O. F.

Estimation of Sulphur in Pyrites. By Thomas S. Gladding (J. Amer. Chem. Soc., 1895, 17, 397—401).—A reply to Lunge (this vol., ii, 291), stating that the author's modifications of his process are absolutely necessary to get accurate results.

L. DE K.

Estimation of Sulphur in Iron and Steel. By LOUIS CAMPREDON (Compt. rend., 1895, 120, 1051—1054).—2.5 to 10.0 grams of the metal is dissolved in 100 c.c. of sulphuric acid (1:5) or hydrochloric acid (1:3) in a flask previously filled with carbonic anhydride, and connected with two apparatus supplying hydrogen and carbonic anhydride respectively. The mixture of gas evolved by the action of the acid on the metal, with the hydrogen and the carbonic anhydride, is passed through a porcelain tube heated to orange redness or an incipient white heat, and all the gaseous sulphur compounds are thus

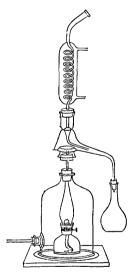
converted into hydrogen sulphide. The gas is then passed into 100 c.c. of a slightly acidified solution of zinc acetate, and the zinc sulphide that is precipitated is mixed with standard iodine solution. the excess of the latter being ascertained by means of standard sodium thiosulphate solution.

The zinc acetate solution is prepared by dissolving 10 grams of zinc oxide in 25 c.c. of glacial acetic acid, diluting to about 500 c.c. adding sufficient ammonia to redissolve the precipitate which forms at

first, and then slightly acidifying with acetic acid.

To prepare the iodine solution, 7.9 grams of purified iodine, together with 25 grams of potassium iodide, is dissolved in 1000 c.c. of water. 1 c.c. = 0.001 gram of sulphur. The thiosulphate solution contains 10 grams of sodium thiosulphate and 2 grams of ammonium carbonate per litre.

Estimation of Sulphur in Petroleum. By Friedrich Heusler (Zeit. angw. Chem., 1895, 285—286).—The apparatus (see illustration) consists of four parts: a small petroleum lamp with its chimney, a reflux condenser, and a special connecting piece which causes the



condensed liquid to run into a receiver by means of a small funnel. The wide top end of the coiled cooling tube is closed by a doubly-perforated stopper; through one opening passes a tube connected with a suitable aspirator; through the other one is introduced a capillary angular syphon through which drops a solution of potassium permanganate. This solution first runs over a pad of glass wool contained in the wide upper tube. If the sample is somewhat rich in sulphur, the permanganate will sometimes be rapidly decolorised; in this case it probably does not run in quickly enough.

To carry out an experiment, the lamp (without its glass) is taken out, filled with about 20-30 grams of the sample, and weighed. Then the suction pump and the capillary syphon are put in action, and when the permanganate solution has moistened the whole of the coil, the condenser and connecting piece are lifted up, and the

lighted lamp is fixed to the lamp-glass, which is attached to the top of the bell-jar by means of a perforated cork. The bell-jar is put on to a greased glass plate, the cooler and connecting piece are lowered, and the latter is connected by a glass tube and cork with the jar. a little practice, it will be found easy to so regulate the force of the air current that complete combustion takes place; once set going satisfactorily, the lamp will burn 12 hours, or even longer. lamp is then re-weighed, the loss in weight representing the amount of oil burned. The condenser, connecting piece, and lamp-glass are all rinsed with water, and the washings added to the liquid in the receiver, which should still contain excess of permanganate. After boiling with hydrochloric acid and filtering, barium chloride is added.

L. DE K.

Standardising Sulphuric acid. By F. S. Shiver (J. Amer. Chem. Soc., 1895, 17, 351—354).—Weinig (Abstr., 1892, ii, 145) has recommended standardising sulphuric acid by neutralising it with ammonia, evaporating to dryness, and finally weighing the ammonium sulphate.

The author states that excellent results may be obtained by this process, but as some ammonia is liberated during the evaporation, it is advisable to moisten the dry residue with ammonia of 0.96 sp. gr., and to again evaporate to dryness. Before weighing, the ammonium sulphate is dried at 110–120°.

L. DE K.

Assay of Fuming Sulphuric acid. By Georg Lunge (Zeit. angw. Chem., 1895, 221—222).—The total acidity of fuming sulphuric acid is generally estimated by means of standard soda, from which is then deducted the acidity due to the sulphurous acid, which is estimated as usual with standard iodine. This process may, however, lead to grave errors.

The indicator used is not a matter of indifference; phenolphthaleïn is not to be recommended, as the soda nearly always contains carbonate, and litmus is out of the question on account of the sulphurous acid. The only good indicator is methyl-orange, but it must be remembered that when using this reagent, neutrality is reached, not when the whole of the sulphurous acid is converted into the neutral sulphite, but as soon as the acid sulphite is formed.

Chemical and Toxicological Properties of Hydroxylamine. By Adalberto Pasquali (Chem. Centr., 1894, ii, 957-958; from Boll. Chem. Farm., 1894, 19).—Angeli's test for hydroxylamine with sodium hydroxide and nitroprusside is well known. Another delicate test is to boil the solution of hydroxylamine hydrochloride with copper sulphate, when nitrous oxide is evolved and cuprous chloride precipitated. Lead peroxide is changed into lead hydroxide, or lead chloride or sulphate also accompanied by evolution of nitrous oxide, whilst the solution contains lead nitrate and Magnesium in contact with solutions of hydroxylamine nitrite. liberates hydrogen. Aqueous potash and carbon bisulphide first give a yellow, and then an orange, liquid; basic lead acetate, or lead hydroxide substituted for the potash, give, on warming, a canary-yellow colour, which fades on adding acids, but turns black with potash. hydroxylamine does not affect the usual indicators, its salts may be titrated best in presence of phenolphthalein with standard alkali. new volumetric process is based on the fact that hydroxylamine decolorises an ammoniacal solution of copper sulphate.

As regards its poisonous character, the author found that it only acts in large doses: 7.75 grams of the hydrochloride given to a dog in small portions during nine days did not affect the animal, but 3 grams administered all at once, caused death. There is no difficulty in finding

traces of the poison in bodies after death even after the lapse of a month.

When hydroxylamine poisoning is suspected, the urine should be tested for nitrous acid. L.  $_{\rm DE}$  K.

Volumetric Estimation of Phosphorus in Steel and Cast By WILLIAM A. NOYES and J. S. ROYSE (J. Amer. Chem. Soc., 1895, 129-137).—Two grams of the sample is put into a 500 c.c. flask, 50 c.c. of nitric acid added, and heat applied until solution is complete; 10 c.c. of a 1.25 per cent. solution of potassium permanganate is then poured in, and the boiling continued until the pink colour disappears. Ferrous sulphate is added, with shaking, until the liquid clears, and, after cooling to 50°, 8 c.c. of ammonia of 0.9 sp. gr. is added, the stopper inserted, and the precipitate redissolved by The solution is then heated as many degrees above or below 60° as the molybdate solution (100 grams of molybdic acid, 400 c.c. of ammonia, 1000 c.c. of nitric acid, sp. gr. 1.2) is below or above 27°; 60 c.c. of this solution is added, the stopper is inserted, and the whole shaken, best with a machine, for five minutes. another five minutes, the molybdate precipitate is collected on a filter of fine texture, and washed with solution of hydrogen ammonium sulphate (27.5 c.c. of ammonia of 0.96, 24 c.c. of sulphuric acid, and 500 c.c. of water) until the washings are no longer coloured by hydrogen sulphide. The precipitate is now dissolved in 12 c.c. of ammonia of sp. gr. 0.96, the filter is washed with 100 c.c. of water, 80 c.c. more water is added, and then 10 c.c. of sulphuric acid.

The solution is passed through a Jones' reductor containing zinc, no air being allowed to pass through during reduction or the washing, and the filtrate is at once titrated with permanganate. The phosphorus equivalent is found by multiplying the iron equivalent of the ermanganate by 0.01538.

L. DE K.

Estimation of Phosphoric acid by means of Ammonium Molybdate. By Hanns von Jüptner (Chem. Centr., 1894, ii, 813—814; from Österr. Zeit. Berg. Hütt., 42, 471—473).—The author has found that tartaric acid even in large excess does not prevent the complete precipitation of phosphoric acid by molybdate solution. The addition of tartaric acid to the molybdate solution or to the phosphate is therefore to be recommended to prevent the contamination of the yellow precipitate with ferric compounds.

L. DE K.

Estimation of Phosphoric acid by the Molybdic acid-Magnesia Process. By Rudolf Dr Roode (J. Amer. Chem. Soc., 1895, 43—46).—The author has proved that at 65° the precipitation of phosphoric acid by the ordinary molybdate solution is complete in five minutes. In analysing phosphates, the author has found it advantageous to add a definite quantity of sodium phosphate solution, the results then being more accurate. The weight of magnesium pyrophosphate yielded by this solution is, of course, deducted from the actual weight. Or, the ignited magnesia precipitate is

dissolved in nitric acid and reprecipitated with molybdate solution, and finally with magnesia mixture; in this case, there is no need for adding sodium phosphate. The author also recommends working on fairly large quantities of substance.

L. DE K.

Estimation of Phosphoric acid. By H. Pemberton (J. Amer. Chem. Soc., 1895, 178—181)—The molybdate solution should be a lded slowly so as to get the yellow precipitate in a crystalline and consequently purer condition. The precipitate is best treated according to the volumetric method, which is quite as trustworthy as the gravimetric process. If titrated with standard alkali, the indicator should be phenolphthalein, not methyl-orange.

L. DE K.

Preparation of Thioacetic acid and its Use in Toxicology. By N. TARUGI (Gazzetta, 1895, 25, i, 269-273; compare Schiff and Tarugi, this vol., ii, 84).—The best method of preparing thioacetic acid for analytical purposes is a slight modification of that described by Kekulé and Linnemann (Annalen, 123, 278), which consists in cautiously distilling phosphorus pentasulphide (300 grams) with glacial acetic acid (108 grams) over a naked flame from a 2-litre flask, pellets of glass (100 grams) being added to prevent frothing; the thioacetic acid may be collected until the thermometer registers 100°, and after one redistillation—collecting the fraction boiling at 90-95°-is perfectly free from arsenic, and may be at once used in toxicological investigation for the precipitation of arsenic. is dissolved in water (2 parts) with the aid of a little ammonia, and the solution thus obtained is boiled with the arsenical liquid; the arsenic is immediately deposited as sulphide, which is collected and examined in Marsh's apparatus. W. J. P.

Separation of Arsenic from other Elements by means of Methylic Alcohol and Hydrogen Chloride. By CARL FRIEDHEIM and PAUL MICHAELIS (Ber., 1895, 28, 1414—1422).—The authors recommend the use of methylic alcohol instead of ferrous chloride in E. Fischer's method for the estimation of arsenic (Abstr., 1881, 195). The general method of procedure is as follows:—

A distilling flask of about 250 c.c. capacity is used, and is fitted with a ground head which is fused to the condenser; a small separating funnel is also ground into the head, and reaches to the bottom of the flask. The receivers are also united to the condenser by means of ground joints. The solution of the substance to be analysed is placed in the flask, and 50 c.c. of methylic alcohol is added; 20 c.c. of concentrated nitric acid is poured into the first receiver, and the others are moistened with distilled water. The mixture in the flask is then saturated with dry hydrogen chloride, the separating funnel serving to keep the methylic alcohol from running back into the drying bottle; during the operation, the flask is kept cool by means of cold water, and, after the solution is completely saturated with hydrogen chloride, it is heated on the water bath while a slow stream of the gas is kept passing through the liquid. If much arsenic is present the operation must be repeated two or three times. Fresh methylic alcohol is

added by means of the separating funnel, and the saturation and distillation are repeated. The distillate, after all the arsenic has passed over, is poured into a porcelain dish and diluted with water; 20—30 c.c. of concentrated nitric acid is added, and, after the vigorous evolution of chlorine has ceased, the whole is evaporated down on the water bath to about 100 c.c. Another 20—30 c.c. of concentrated nitric acid is added, and the liquid is then evaporated down to dryness; the residue is extracted with water, filtered, and precipitated with magnesia mixture. Details are given (1) of estimations of pure arsenic; (2) of the separation of arsenic and vanadic acid; (3) of the separation of arsenic and molybdic acid; (4) of the estimation of arsenic and tungstic acid.

In order to completely separate arsenic and vanadic acid, it is necessary to reduce the latter to V<sub>2</sub>O<sub>4</sub>, by warming for a short time with sulphurous acid, and then to distil in the usual way, as otherwise

part of the vanadium passes over with the arsenic.

In order to prevent part of the molybdenum from passing over with the arsenic, it is necessary to dilute the methylic alcohol with water for the first operation. Arsenic acid in the presence of tungstic acid cannot be estimated by this method, as 2—3 per cent. of the arsenic always remain behind in the distilling flask. The author recommends the estimation of the two together by means of mercurous nitrate solution (see Gibbs, *Proc. Amer. Academy*, 16, 134), then the estimation of the tungsten separately, and the calculation of the arsenic from the difference.

J. J. S.

Two New Colorimeters for Carbon Estimation. By WALTER G. McMillan (Chem. Centr., 1895, i, 173-174; from Stahl u. Eisen, 1894, 1073-1075).—The first apparatus consists of two graduated cylinders, one of these containing the solution to be tested, and the other the standard solution used for comparison; the second cylinder being connected by a side tube with a reservoir containing a float. By depressing the latter, the depth of the column of liquid in the comparison tube can be adjusted so as to correspond in colour with the solution which is being tested. A milk-white stopper is placed level with the zero in each tube, and a movable shutter facilitates the reading of the graduation. In the second form of apparatus, the standard liquid and that for comparison are placed in tubes the upper part of which is expanded in the form of a basin. These are enclosed in a blackened case with a long slit in the bettom, to which light is directed by a reflector, and in each, another tube is made to slide and regulate the depth of liquid. The sliding tubes are provided with an index working on a scale, and to begin with are depressed till the liquid is forced into the basin-like neck of the containing tubes, and a white disc only appears on observation. This is taken as zero. tube is then raised until a suitable colour and depth of liquid is obtained, and the other is adjusted to correspond. L. DE K.

Analysis of Bone-black. By W. D. Horne (J. Amer. Chem. Soc., 1895, ii, 51—55).—The author restricts the analysis to the estimation of moisture, carbon, calcium carbonate, sulphate, and sulphide, also

iron and alumina. The analytical details present, on the whole, no novel features. The density is determined by filling a weighed 100 c.c. flask, with sloping sides, with the sample and re-weighing; this gives the sp. gr. of the loose char. The flask is then gently tapped, and more char is added; this gives the sp. gr. of the packed sample.

To determine the relative durability of sample under continued friction, the following test is recommended: 25 grams of the sample between 16—24 grist is thrown on a sieve with circular holes one-fiftieth of an inch in diameter, the sieve shaken backwards and forwards 10 times, tapped three times, and the shaking and tapping repeated twice. This drives the dust through, and it is weighed. Dust and char are then both put into a cylinder of tinned iron, 4 inches in diameter and 2 inches deep, along with six glazed porcelain marbles, five-sixths of an inch in diameter, and jointly weighing 74.66 grams. The can is now shaken backwards and forwards with a slightly rotatory motion 200 times, the marbles are removed, and the char is again sifted. The increase in the weight of dust will then give an idea as to the quality of the sample.

Absorption Apparatus for Elementary Analysis. By Julius Bredt and Wilhelm Posth (Annalen, 1895, 285, 385—386).—The authors advocate the employment of soda-lime as a substitute for potassium hydroxide.

M. O. F.

Estimation of Potash in Kainite. By Rudolf de Roode (J. Amer. Chem. Soc., 1895, ii, 85).—The author recommends evaporating the aqueous solution of kainite with the addition of platinum chloride, without any attempt at removing sulphates, lime compounds, &c. The residue is first extracted with alcohol to remove the excess of platinum chloride, and then with a solution of ammonium chloride to remove the impurities; a pure potassium platinochloride is thus obtained. The test-analysis was slightly higher than the usual result, but this is only natural, as the new process is not interfered with by occlusion of potash in the various precipitates, or by loss from decrepitation or volatilisation.

L. DE K.

Estimation of Potash in Manures. By W. E. Garrigues (J. Amer. Chem. Soc., 1895, ii, 47—51).—Ten grams of the sample is well mixed with strong sulphuric acid, in a platinum dish, and the whole is then gradually ignited until all the organic matter has been burnt off. The mass is now powdered, washed into a 500 c.c. flask with 250 c.c. of hot water, boiled for half an hour, and a 10 per cent. solution of barium chloride is cautiously added until no further precipitate is produced. A drop of phenolphthalein is introduced, and then, drop by drop, a solution of sodium carbonate until a faint, permanent rose colour is obtained. After cooling, the liquid is diluted to the mark, and 50 c.c. (1 gram) of the filtrate is used for the potash estimation. This is done, as usual, by evaporation with platinum tetrachloride and a drop of hydrochloric acid.

When analysing potash salts, the evaporation with sulphuric acid may be omitted.

L. DE K.

Estimation of Potassium Sulphate in Wine. By L. Hugouneng (J. Pharm., 1895, [6], i, 349—354).—The author has proved that wine contains organic sulphur compounds, which afterwards are found in the ash as sulphates, and so increase the quantity of potassium sulphate by 30—40 per cent. To get a correct result, the estimation of the sulphuric acid must be made in the original sample, and not on the acid solution of the ash. The various sugars, tartrates, &c., contained in the wine have no particular influence on the accuracy of the result.

Reaction between Zinc Sulphate and Potassium Hydroxide. By C. E. LINEBERGER (J. Amer. Chem. Soc., 1895, 17, 358—360).

—In works on analytical chemistry, it is customary to represent two molecules of potassium hydroxide as necessary to precipitate the zinc from one molecule of zinc sulphate. The precipitate is then supposed to redissolve by adding another two molecules of potash.

The author has experimentally proved that these ideas are quite erroneous, and that the reaction depends on temperature, dilution, and the relative masses of the components. In one experiment, 1.62 mols. of potassium hydroxide were sufficient to completely throw down a molecule of zinc, and in another trial not two, but 13.2 mols. of alkali were necessary to redissolve the molecule of zinc hydrate.

L. DE K.

Volumetric Estimation of Metals. By Henri Lescoeur (Bull. Soc. Chim., 1895, [3], 13, 280—281).—The author has for some years past used a process for the estimation of zinc in presence of free acid very similar to that described by Barthe (this vol., ii, 371), methylorange being substituted for the tincture of hollyhock. The precipitate obtained in this modified process is not, however, a basic sulphate, but the pure oxide of the metal.

Jn. W.

Estimation of Lead. By Andreas Kreichgauer (Zeit. anorg. Chem., 1895, 9, 89—125; see also Abstr., 1894, ii, 217).—The paper contains a critical account of the electrolytic estimation of lead, and the results obtained with three different natural sulphides of lead, when analysed by the electrolytic method, by precipitation with bromine, and as sulphate, are compared. The precipitation with bromine is most convenient when the ores contain much antimony or zinc. The electrolytic method is adapted for products containing only small quantities of antimony, and especially when the product can be dissolved directly in nitric acid, and this process is generally the most accurate. The precipitation as sulphate is only advantageously employed when lead alone is present.

E. C. R.

Quantitative Analysis of Galena. By Paul Jannasch and H. Kammerer (Ber., 1895, 28, 1409—1411).—The authors recommend the following method for the analysis of galena. 0.7—0.75 gram of the finely powdered mineral is moistened with dilute nitric acid, and allowed to remain for several minutes, 10 c.c. of concentrated acid is then added, and the whole is heated on the water bath, and evaporated; nitric acid and water are then added, together with

10-15 drops of bromine, and the mixture is heated with continual stirring until all the sulphur is oxidised to sulphuric acid. In order to decompose any bromate which may be formed, the mixture should be evaporated to dryness three times with concentrated nitric acid. The residue is boiled with 60 c.c. of water and 20 c.c. of concentrated hydrochloric acid, and filtered from the insoluble residue (SiO<sub>2</sub>, &c.), which is ignited and weighed. To estimate the lead, the filtrate is heated to boiling, and the clear solution poured at once into a mixture of 25 c.c of water, 50 c.c. of hydrogen peroxide, and 50 c.c. of concentrated ammonia; the lead is thus thrown down as a yellowish-red, slightly crystalline precipitate, the composition of which will be The mixture is allowed to remain for several determined later. hours, with occasional stirring, the precipitate is then collected, washed with cold water, dried, and weighed in a platinum crucible as The filtrate is evaporated down, until the smell of lead oxide. ammonia has disappeared; 5 c.c. of concentrated hydrochloric acid and 5 c.c. of alcohol are added, the mixture again warmed, in order to destroy any persulphate which may be present, and the sulphuric acid is then precipitated by means of barium chloride. Impurities such as copper, nickel, zinc, and arsenic can be estimated in the filtrate from the barium sulphate.

Wet Copper Assay. By R. S. Dulin (J. Amer. Chem. Soc., 1895, 17, 346-351).—The most popular (American) assaying processes in the wet way are the electrolytic method, and the process by which the copper is precipitated by potassium iodide and the liberated iodine titrated, but these processes can only be employed in the absence of interfering metals or acids. The time-honoured cyanide process gives, however, excellent results, provided the copper is first precipitated with aluminium.

The copper ore is treated according to the directions given in Furmen's Manual of Assaying, the resulting solution being practically free from lead and silver; when boiled with strips of aluminium foil, the copper is completely precipitated, and if the boiling is then stopped at once, scarcely any cadmium will come down. The copper deposit is washed, dissolved in nitric acid, mixed with excess of ammonia, and titrated with potassium cyanide solution; in standardising the latter, as nearly as possible the same amount of copper, nitric acid, ammonia, &c., should be used in order to get trustworthy results.

Quantitative Separation of Metals in Alkaline Solution by Hydrogen Peroxide. By Carl Engels (Zeit. anorg. Chem., 1895, 9, 78).—Regarding the paper by P. Jannasch and A. Röttgen with this title (this vol., ii, 331), the author states that he has been for some time engaged in the electrolytic separation of manganese from iron and copper in the presence of hydrogen peroxide and an organic compound. 0.5 gram MnO<sub>2</sub> can be estimated quantitatively by this method in one hour.

E. C. R.

Electrolytic Estimation of Manganese. By MAX Gröger (Zeit. angw. Chem., 1895, 253—254).—Electrolytically deposited manganese

peroxide has, according to Rüdorff, the composition, MnO<sub>2</sub>,H<sub>2</sub>O, when dried at 60°; using this formula, about 99 per cent. of manganese present is recovered during an analysis. The author has, however, proved that the precipitated manganese is not entirely in the state of dioxide, and if estimating it by means of potassium iodide and sodium thiosulphate, only 94—96 per cent. of the manganese will be found.

L. DE K.

Methods for Estimating Manganese. By W. S. Thomas (J. Amer. Chem. Soc., 1895, 17, 341—346).—The author has investigated some volumetric methods for estimating manganese with the object of finding out which process is most suitable for technical purposes.

The conclusion is, that the best method is the one proposed by Volhard, namely, titration of the manganous salt by means of potassium permanganate in presence of zinc oxide. Low's oxalic acid process, although theoretically perfect, has entirely failed in the author's hands.

L. DE K.

Estimation of Iron in Ores, Slags, &c. By Hans von Jüptner (Chem. Centr., 1894, ii, 815; from Österr. Zeit. Berg Hütt., 42, 469—470).—0.5 gram of the sample is mixed with 1 gram of magnesium powder and ignited for 5—10 minutes in a covered porcelain crucible; if the substance is very rich in ferrous oxide, 4—6 grams of magnesium should be used. The magnesium should be tested as to the amount of iron it contains.

The contents of the crucible is dissolved in dilute sulphuric acid and the iron estimated with standard permanganate. L. DE K.

Zimmermann-Reinhardt's Method for Estimating Iron in Iron Ores. By C. T. Mixer and H. W. Du Bois (J. Amer. Chem. Soc., 1895, 17, 405—411).—The ore is dissolved in hot hydrochloric acid with the addition of stannous chloride, solution being complete in a few minutes. The excess of stannous chloride is removed by the addition of mercuric chloride, and the iron is then at once titrated with permanganate solution. To prevent injurious action of the hydrochloric acid on the permanganate, a solution of manganous sulphate also containing sulphuric and phosphoric acid is added before titration. The permanganate is checked by means of a standard iron ore, the composition of which has been ascertained in a variety of ways.

The authors, after a good many trials, strongly recommend this method for technical purposes.

L. DE K.

Analysis of Steel. By H. K. Bamber (Chem. Centr., 1894, ii, 815; from Stahl u. Eisen, 14, 872).—The sample is dissolved in dilute nitric acid, nearly neutralised with sodium hydroxide, and the liquid evaporated to dryness; the mass is then treated with 50 c.c. of 10 per cent. aqueous soda, again evaporated to dryness, and powdered. The powder is lixiviated with 0.5 per cent. aqueous soda, which then contains the various minor constituents such as phosphorus, arsenic, sulphur, chromium, vanadium, molybdenum, &c. L. DE K.

Estimation of Iron in Urine. By LOUIS LAPICQUE (Bull. Soc. Chim., 1895, [3], 13, 281—285).—See this vol., ii, 407.

Estimation of Nickel in Nickel-Steel. By EDWARD D. CAMPBELL and W. H. Andrews (J. Amer. Chem. Soc., 1895, ii, 125-129). Preliminary Treatment.—One gram of the sample is boiled in a 500 c.c. Erlenmever flask with 25 c.c. of nitric acid (sp. gr. 1.20) until dissolved, meanwhile, 13 grams of sodium pyrophosphate is dissolved in 75 c.c. of warm water, filtered, and added to the cooled nitric acid solution. A 20 per cent. solution of sodium carbonate is now slowly poured in until the ferric pyrophosphate has just dissolved. and the liquid attains a dull, olive-green colour; excess of soda. betraving itself by a red colour, must be carefully avoided. liquid is now filtered through asbestos into a 500 c.c. Erlenmeyer flask, a solution of 2 grams of potassium xanthate in 25 c.c. of water is added, and the flask is stoppered and well shaken for about 10 minutes. The nickel is completely precipitated as xanthate, together with any copper, but is perfectly free from manganese and almost free from iron; the precipitate, collected on an asbestos filter. must be washed with a 1 per cent. solution of the reagent, which. in solution, does not keep more than 15 minutes.

The precipitate is dissolved off the filter by allowing 20 c.c. of nitric acid (10 c.c. of water, 10 c.c. of fuming acid) to slowly drop on to it: the filter is first washed a few times with hot water, then with 5 c.c. of dilute sulphuric acid (2-3), and finally again with hot water. The solution is now rapidly boiled in an Erlenmeyer flask until the nitric acid is completely expelled, and fumes of sulphuric acid begin to be visible. After cooling, the residue is dissolved in 25 c.c. of water, heated nearly to boiling, a current of hydrogen sulphide passed through it to precipitate the copper, and the whole filtered. filtrate is boiled to expel the gas, and the iron, oxidised by means of a few drops of hydrogen peroxide, or by a few particles of sodium dioxide, is at once precipitated by ammonia; the precipitate must. however, after washing, be redissolved in 5 c.c. of the dilute sulphuric acid, and again precipitated hot with ammonia so as to completely free it from nickel. In the united filtrates, the nickel may then be determined either by electrolysis or by titration.

Electrolytically.—The solution, mixed with 30 c.c. of 10 per cent. ordinary sodium phosphate and 25 c.c. of strong ammonia, is diluted to about 175 c.c., and placed in a platinum dish of 200 c.c. capacity; the nickel is then deposited on the platinum by means of a current of 0.14 ampère per 100 sq. cm. area of the dish, the electrodes being

about 0.5 cm. apart.

Volumetrically.—To the liquid is added 5 c.c. of a solution of silver nitrate (0.05 per cent.), then 5 c.c. of a 2 per cent. solution of potassium iodide; solution of potassium cyanide (0.5 per cent.) is now run in until all the nickel has passed into double cyanide, which is indicated by the disappearance of the silver iodide. The cyanide solution is standardised by means of pure nickel wire, and a blank experiment is made to ascertain the amount of cyanide required to dissolve the silver iodide.

L. DE K.

Separation of Metals with a Current of Carbonic Anhydride containing Bromine. By Paul Jannasch, Ed. Rose, and R. Nieder-HOFHEIM (Zeit. anorg. Chem., 1895, 9, 194-204).—Separation of Bismuth and Cobalt.—For the test experiment, a mixture of metallic bismuth with cobalt ammonium sulphate was employed. A weighed quantity of the finely powdered substance, dried in a current of carbonic anhydride, whereby the greater part of the ammonium salt is eliminated, is mixed with about 10 times its weight of pure sulphur, heated in a current of dry hydrogen sulphide, and allowed to cool. The product is again heated with sulphur, and, after the excess of sulphur has sublimed, it is allowed to cool, and is treated with a current of dry carbonic anhydride saturated with bromine; meanwhile the tube containing the mixture is cautiously heated. Sulphur bromide sublimes at first, and then bismuth bromide, and the temperature must be regulated so that no lustrous spangles of cobalt bromide are formed; the volatile products are collected in dilute nitric acid. The green residue of cobalt bromide is dissolved in water, except a small black residue, which requires nitric acid to dissolve it; it contains ro bismuth. The solution, heated to boiling, is precipitated with sodium hydroxide, and the cobalt weighed either as Co<sub>3</sub>O<sub>4</sub> or as metallic cobalt. The nitric acid solution containing the bismuth is evaporated to dryness on the water bath, the residue dissolved in dilute nitric acid, and the bismuth precipitated with an excess of ammonia and hydrogen peroxide. The results obtained are accurate.

The separation of bismuth and nickel is performed in the same way as above. It is very difficult to dissolve the residual crystalline nickel compound in water, but it easily dissolves on the addition of acid.

Separation of Tin and Antimony from Lead and Copper.-The method is similar to that described above. The mixture of metals is weighed into a porcelain boat and heated in a tube of hard glass. Before treating with bromine, the sample to be analysed is heated with sulphur containing iodine. The bromine must be free from chlorine and water, and the carbonic anhydride from hydrochloric acid. In the separation of tin and lead, the residue of lead bromide can be weighed as such; it should give a clear solution in fresh chlorine water. In the separation of tin and copper, the solution containing the tin is first evaporated to dryness on the water bath, and is then heated in an air bath to drive off the sulphuric acid; the tin oxide obtained is heated until the weight is constant. The residue of copper, which is not pure cupric bromide, but contains cuprous bromide, is dissolved in dilute nitric acid, the solution evaporated to dryness, and the residue of nitrate ignited, and weighed; or the nitric acid solution is at once precipitated with sodium hydroxide. separation of antimony from lead is very similar to that of tin from lead, but great care must be taken that no antimony sulphide is volatilised during the treatment with sulphur. The antimony solution is evaporated and freed from sulphuric acid as in the case of tin, it is then evaporated to dryness two or three times with fuming nitric acid, ignited, and the antimony weighed as antimony metantimoniate. Or the antimony is precipitated directly from the nitric acid solution

as sulphide, the precipitate washed with a solution of ammonium nitrate containing hydrogen sulphide, dried at 80—90°, and then treated with fuming nitric acid, and the antimony weighed as dioxide. The separation of antimony and copper is performed in a similar way.

E. C. R.

Quantitative Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide.—12th Paper. By Paul Jannasch and H. Kammerer (Ber., 1895, 28, 1407—1409).—(1) Separation of Manganese and Silver.—Silver nitrate (0.7—0.8 gram) and manganese-ammonium sulphate (0.7 gram) are dissolved in a mixture of water (10 c.c.) and concentrated nitric acid (10 c.c.); the solution thus obtained is poured into a mixture of water (20 c.c.), hydrogen peroxide (50 c.c.) and concentrated ammonia (40 c.c.) and the whole is heated on the water bath during 10—12 minutes. The precipitate is collected and washed, first with a mixture of water (8 parts by vol.), hydrogen peroxide (17 parts) and ammonia (17 parts), and finally with hot water. After ignition, the manganese is weighed as Mn<sub>3</sub>O<sub>4</sub>. The filtrate is heated on the water bath until the smell of ammonia has disappeared, nitric acid is added and the silver estimated in the usual way as chloride.

(2) Separation of Bismuth and Cobalt - Cobalt ammonium sulphate (0.5 gram) and metallic bismuth (0.35 gram) are heated on the water bath with concentrated nitric acid (10 c.c.) and water (10 c.c.), until all is dissolved. The solution, after the addition of concentrated nitric acid (10 c.c.), is poured into a freshly prepared mixture of water (20 c.c.), hydrogen peroxide (50 c.c.), and concentrated ammonia (50 c.c.). The bismuth precipitate, which still contains a trace of cobalt, is collected and washed, first with a mixture of water, hydrogen peroxide and ammonia (see above), then with dilute ammonia, and finally with hot water. It is now dissolved in hot, dilute nitric acid, and concentrated acid is added in order to make up the total amount of concentrated acid present to The precipitation is again repeated, and after washing as before, the precipitate is dried at 90°, and ignited and weighed in a platinum crucible as bismuth oxide. The filtrate containing all the cobalt is evaporated to dryness, and the residue heated in an air bath to drive off all ammonium salts; it is then dissolved in water to which hydrogen peroxide and a few drops of hydrochloric acid have been added, the solution heated to boiling, and the cobalt precipitated by the addition of a slight excess of pure sodium hydroxide, together with bromine; the precipitate is dried, ignited and weighed as Co<sub>3</sub>O<sub>4</sub>. The cobalt may also be directly precipitated from the ammoniacal filtrate by means of ammonium sulphide.

J. J. S.

Estimation of Paraffin in Crude Anthracene. By FRIEDRICH HEUSLER and Jos. HERDE (Zeit. angw. Chem., 1895, 253).—The process is based on the fact observed by the authors that all the constituents of crude anthracene, paraffin excepted, are soluble in fuming nitric acid.

Two grams of the sample is put into a 150 c.c. flask, cooled in iced water, and very gradually mixed with 25 c.c. of fuming nitric acid; the mixture is then heated for a while on the water bath until the paraffin has melted, and again cooled. The solid mass is now collected on an asbestos filter, and after being washed with fuming nitric acid until this no longer becomes milky on adding water, the acid is removed by washing with water. The paraffin is first rinsed with alcohol into a weighed porcelain dish, and the spirit evaporated; in the meantime, the remaining paraffin is dissolved in hot ether, and this solution is also evaporated in the same dish. Before weighing, the paraffin is finally dried at 105—110° for half an hour.

L. DE K.

Detection of Potassium Cyanate in small quantity, in Potassium Cyanide. By Edward A. Schneider (Ber., 1895, 28, 1540—1541).—The method is based on the formation of the deepblue potassio-cobalt cyanate, Co(CNO), 2KCNO. The potassium cyanide in the liquid under examination, which must be as concentrated as possible, is decomposed by means of a current of carbonic Alcohol (90-95 per cent.) is added, to precipitate the potassium carbonate, and the filtrate treated with a few drops of acetic acid, and then with cobalt acetate solution. In this way, the presence of 0.0033 gram of potassium cyanate in 100 c.c. of liquid may be detected. The decomposition of 3 grams of potassium cyanide (10 per cent. solution) occupies about 45 minutes. When larger quantities have to be employed, the salt is dissolved in the smallest possible quantity of water and mixed with alcohol so as to precipitate most of the cyanide, the filtrate being then treated with carbonic anhydride as above. The presence of 1-0.35 parts of cyanate in 100 parts of cyanide is easily detected. Aqueous solutions of potassium cyanate are less stable than alcoholic, but the former do not decompose so readily as is generally stated, in one experiment 50 c.c. of potassium cyanate solution (1 per. cent.) gave the cobalt reaction after being rapidly boiled for an hour; heating, even of alcoholic cyanate solutions intended for analysis, should be avoided.

J. B. T.

Discrimination between Lactose and Glucose in Adulterated Peptones. By L. Ruizand (J. Pharm., 1895, [6], i, 232—233).— Five grams of the sample is dissolved in 45 c.c. of water and 5 c.c. of hydrochloric acid, heated for two hours in a water bath at 70°, and neutralised with aqueous soda; the liquid, which may now contain glucose and galactose, is mixed with 12 grams of sodium acetate and 8 grams of phenylhydrazine hydrochloride, and again heated for an hour. The whole is then filtered boiling; phenylglucosazone is insoluble, but the galactose compound is soluble, and crystallises out on cooling; after washing and recrystallising from hot water, it is dried, and its melting point is taken; this should be 188—191°.

A more simple test is based on the fact that neutral copper acetate is reduced by glucose, but not by lactose. If, however, the latter is

first inverted by treating with acid, as described, it also reduces the copper.  ${\rm L.} \ \ {\rm DE} \ \ {\rm K}.$ 

Identification and Estimation of Carbohydrates in Milk. By ALEXANDER WYNTER BLYTH (Analyst, 1895, 20, 121—126)— The paper is chiefly devoted to an improved process of recognising and estimating added sugars in milk; 25 c.c. of milk is diluted to 50 c.c. with water, and acetic acid is added drop by drop, until the casein separates. After heating to boiling, the liquid is whirled in a glass cylinder by the aid of a centrifugal machine. The bulk of the proteid and fatty matters separate, and adhere to the bottom of the cylinder, and the supernatant liquid is easily filtered. The filtrate may be examined polarimetrically, and the reducing sugars estimated by the copper cyanide process.

To identify foreign sugars with certainty, it is well to prepare the osazone; in this case, the filtrate is evaporated down to 30 c.c., and the filtered liquid mixed with 2 grams of sodium acetate, and 1.5 gram of phenylhydrazine hydrochloride. After warming for an hour and a half in a water bath, it will be found that, on cooling, the liquid becomes almost solid; the crystals are collected, pressed between blotting paper, and dried in a water oven. The osazone is then boiled with absolute alcohol (30-40 c.c.), and when dissolved allowed to stand over night; if glucose or invert sugar is present in the milk, well defined crystals will separate. The alcoholic filtrate is now heated to boiling on the water bath, water is added until a slight turbidity shows itself, and the whole is then allowed to slowly evaporate, when the osazone will crystallise out. If entirely due to lactose it looks under the microscope as aggregations of warty masses, but if partly due to glucose, bundles of needle-shaped crystals will be noticed.

Melitriose (Raffinose) and its Estimation. By A. BAU (Chem. Zeit., 1894, 18, 1794—1799).—After a detailed historical account of the discovery and investigation of raffinose, the author describes his investigation of its behaviour towards yeast, and his experiments on its estimation. Raffinose crystallises in long, pointed needles, the specific refractive power  $[\alpha]_D = +1040$ , and it yields an undecacetyl These properties are given incorrectly in many textbooks. The experiments with yeast were all performed with pure cultures and sterilised solutions; the results show that it is quite unfermentable with bottom fermentation yeast, and only partially so with top fermentation yeast, as the melibiose which is formed undergoes no change. From experiments with Monilia candida, it is almost certain that raffinose is not directly fermentable. The presence of raffinose in barley has been demonstrated by the preparation of the osazone from the fermented and purified extract. Of the various methods proposed for the estimation of raffinose, the fermentation one gives, as a rule, the most satisfactory results; the solution of the substance (10-12 per cent.) is mixed, if needful, with nutritive solution, sterilised, and divided into four portions, two of these are treated with top fermentation, two with bottom fermentation yeast, VOL. LXVIII. ii.

pure cultivations being employed; the time required for fermentation is at least 10—14 days; the liquid is made up to its original weight with sterilised water, filtered, and the filtrate analysed (polarisation, cupric reducing power, and extractive matter), the difference between the extract of the two fermentations, multiplied by 1.737, gives the amount of raffinose. No correction is necessary for the yeast. Reference is made to E. Fischer and Thierfelder's experiments on the fermentability of galactose (Abstr., 1894, i, 486).

J. B. T.

Estimation of Starch. By P. L. Hibbard (J. Amer. Chem. Soc., 1895, ii, 64-68).—A weighed quantity of the sample, containing at least 0.5 gram of starch, is placed in a flask with 50 c.c. of water, and 1-2 c.c. of malt extract, prepared by soaking coarsely pulverised malt with water containing 20 per cent. of alcohol. The mixture is at once heated to boiling, shaking frequently, to prevent formation of insoluble clots. If, however, the material is poor in starch, the addition of malt is at first omitted; the liquid is boiled for a minute, and when again cooled down to 50-60°, 2-3 c.c. of malt solution is added; it is then again slowly heated to boiling, and tested for starch with iodine. When all the starch has disappeared, the mixture is cooled, made up to a definite bulk, and filtered through fine muslin; an aliquot part of the filtrate, corresponding with about 0.3 gram of starch, is then placed in a 100 c.c. flask with 5 c.c. of 30 per cent. hydrochloric acid, and sufficient water to make up to 60 c.c. solution is now boiled gently for 30 minutes on a sand bath, then cooled, nearly neutralised with aqueous soda, and the dextrose estimated with Fehling's solution. A blank experiment is, of course, made to ascertain the amount of dextrose yielded by the malt extract. L. DE K.

Detection of Formalin. By H. Droop Richmond and L. Kidgell Boseley (Analyst, 1895, 20, 154—156).—Guided by Pulvermacher's researches on compounds of formaldehyde with substituted ammonias, the authors have worked out the following process:—Diphenylamine is dissolved in water with the aid of sulphuric acid; the liquid to be tested (milk for instance) is distilled, the distillate added to the reagent, and boiled. In the presence of formaldehyde, a white, floculent precipitate is deposited which occasionally may be green, due to nitric compounds in the sulphuric acid.

L. DE K.

Estimation of Furfuraldehyde in Pentoses and Pentosans. By B. Welbel and S. Zeisel (Monatsh., 1895, 16, 283—311).—The authors base their method of estimating furfuraldehyde in pentoses and pentosans on the observation that in presence of a 12 per cent. solution of hydrochloric acid, phloroglucinol and furfuraldehyde condense in the cold, and even more readily on heating, forming a dark coloured, insoluble compound. This compound can be collected in a tared asbestos filter, dried at 100—110°, and weighed.

G. T. M.

Detection of Salicylic acid in Wines. By MATTEO SPICA (Gazzetta, 1895, 25, i, 207—216).—The ferric chloride test for salicylic acid, although satisfactory for the examination of beers, is of

less value in the case of wines, as the ether used in extraction takes up small quantities of tartaric, tannic, and acetic acids, together with the salicylic acid, and so masks the colour test.

The author uses a modification of Röse's method by which the wine is extracted with ether, the ethereal solution evaporated, and the residue taken up by light petroleum, in which tartaric acid is insoluble; the ferric chloride test is then applied to the residue obtained on evaporating the petroleum solution. Should the colour obtained be faint, it is well to render the wine alkaline and concentrate before extracting; in order to prevent the repetition of the process thus involved, the residue obtained on evaporating the ethereal solution is warmed with concentrated nitric acid, rendered alkaline with ammonia, and the solution heated with a thread of white wool previously freed from grease by potash and ether. presence of salicylic acid is betrayed by the yellow colour given to the wool by the picric acid produced; the test is not affected by the presence of tartaric, tannic, or acetic acid, and is sensitive to 0.02 milligram of salicylic acid per litre of wine if 10-25 c.c. of the latter is used.

Maumené's Test for Oils. By H. Droop Richmond (Analyst, 1895, 20, 58—59).—The calorimeter used by the author consists of a small, deep beaker fitted inside a slightly larger one by means of a ring of cork; the outer beaker being placed in a tin cup padded with cotton-wool. Its heat capacity is estimated by placing 10 grams of water inside, noting the temperature, and pouring in 25 grams of hot water (of known temperature), and observing the resulting temperature.

The total heat evolved in a Maumené experiment, which the author calls the *relative molecular Maumené figure*, is calculated from the equation

$${\rm R.M.M} = {\rm R} \times \frac{21.5}{x - 78.5} \times \frac{20 + h}{20} \times \frac{19.5}{\rm K},$$

in which R is the observed rise in temperature from 25 grams of oil and 5 c.c. of sulphuric acid, x its percentage of real sulphuric acid (which must not be below  $92^{\circ}$ ), h the heat capacity of the calorimeter in grams of water, and K the potash absorbing figure of the sample,  $19.5^{\circ}$  being taken as the average.

L. DE K.

New Thermal Method for Examining Oils. By Otto Hehner and Charles A. Mitchell (Analyst, 1895, 20, 146—150).—The authors prefer using bromine instead of sulphuric acid when testing oils for rise in temperature.

One gram of the oil is dissolved in 10 c.c. of chloroform and introduced into a vacuum-jacketed test-tube. A delicate thermometer is put in, and, after noticing the temperature, 1 c.c. of bromine is added, and the increase in temperature observed. The authors have tabulated the results of 31 samples of oil and fat. In nearly every case-the iodine absorption figure agreed very well with the rise in temperature, and could be calculated by multiplying the latter by 5.5.

L. DE K.

Gravimetric Estimation of Bromine Absorption of Fats. By Otto Hehner (Analyst, 1895, 20, 49—52).—The author has found that the compounds of fats with bromine may be dried at 125° without loss, and has based on this fact a gravimetric process for determining the bromine absorption of fats.

From 1—3 grams of the sample is introduced into a small wide-mouthed flask and carefully weighed. The fat is dissolved in a few c.c. of chloroform, and bromine is then added until it is decidedly in excess. The flask is heated on the water bath until most of the bromine is driven off, a little more chloroform is added, and the mixture again heated, the chloroform vapour expelling the excess of bromine. The residue is then dried at 125° until the weight is constant.

L. DE K.

Hübl's Iodine Absorption Method. By Julius Ephraim (Zeit. angw. Chem., 1895, 254—259).—The author has investigated the nature of the Hübl's solution (iodine and mercuric chloride dissolved in alcohol), and thinks that, as its action is chiefly due to chloride of iodine, it is more convenient to make an alcoholic solution of iodine monochloride instead. This should contain 16.25 grams of the compound per litre.

L. DE K.

The Amorphous Nitrogenous Organic Compounds in Beer Wort. By N. C. Henrik Schjerning (Zeit. anal. Chem., 1895, 34, 135—147).—It is first shown that one of the statements in the earlier paper (Abstr., 1894, ii, 371) requires correction. The stannous chloride precipitate is not identical with the absolute baryta precipitate (abs. Ba), but with the absolute lead precipitate (abs. Pb = Pb — abs. Ba): the absolute baryta precipitate is therefore the same as Pb — Sn, and is best estimated by subtracting the amount of the stannous chloride precipitate from the amount of the lead acetate precipitate.

The author then proceeds to determine the amount of nitrogen extracted from malt by one hour's mashing at different temperatures, ranging from 25° to 100°, and the proportion of the nitrogen precipitated by each of his four reagents (Ba - or rather Pb - Sn, Sn, Fe, and Ur, loc. cit.), from each of the worts thus obtained; the greatest solubility for the nitrogenous constituents of malt, as well as the highest degree of peptonising is found at about 60°. The amount of ammonia extracted is the same at all temperatures, and is not altered by subsequent boiling of the wort for three hours. The general results seem to support Mulder's hypothesis of the derivation of the amorphous nitrogenous organic compounds in wort from a single highly complex proteïd. The curves representing the changes in the amounts of the different precipitates as the temperature of mashing is varied indicate that the peptones are formed at the expense of the albuminous substances, and the propertone chiefly at the expense of the material which the author has provisionally called "denucleïn."