

# THE ANALYST.

## PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

### ESTIMATION OF MORPHINE IN INDIAN OPIUM.

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(Read at the Meeting, June 4, 1919).

SINCE the lime process for the estimation of morphine in opium was introduced numerous investigators have pointed out its several advantages and defects. Presumably they have not used Indian opium, and it was thought worth while to ascertain to what extent correct results are obtained in the case of this material. At present either the B.P. 1898 or B.P. 1914 process is generally followed, and most of the following experiments are based on them.

When 1 gm. of chemically pure morphine was treated as opium powder for morphine estimation by the B.P. process only 0.95 gm. was recovered; the amount of the alkaloid lost may be present (1) either in the undissolved lime, or (2) in the mother liquor after separation of morphine. In order to determine where it is retained the polarimetric process was resorted to.

The effect of the presence of ammonium chloride, calcium chloride, and ether on the specific rotation of morphine was studied, as the determination of morphine had to be made in the presence of these salts.

Ammonium Chloride.	Morphine Concentration as Hydrochloride.	Polarimetric Reading in Ventzke Scale in 200 mm. Tube.	Specific Rotation of Morphine.
Per Cent.	Per Cent.		
2.5	1	- 7.31	- 126.8°
5	1	- 7.33	- 127.1°
10	1	- 7.34	- 127.3°
20	1	- 7.34	- 127.3°

Calcium Chloride.	Morphine Concentration as Hydrochloride.	Polarimetric Reading in Ventzke Scale in 200 mm. Tube.	Specific Rotation of Morphine.
Per Cent.	Per Cent.		
2.5	1	-7.29	-126.4°
5	1	-7.30	-126.6°
10	1	-7.30	-126.6°
20	1	-6.70	-116.2°
Ether—			
10	1	-7.04	-122.0°

It is thus seen that the results are not seriously affected by the presence of small quantities of the salts, and in the case of an aqueous solution containing the maximum quantity of ether (10 per cent. by volume) the specific rotation may be accepted as  $-122.0^\circ$ . The procedure was as follows: 1.4 gm. of pure morphine was treated with 6 grms. of freshly slaked lime, as in the B.P. 1898 procedure; the undissolved lime was filtered under diminished pressure, dissolved in dilute hydrochloric acid, and made up to 100 c.c.; in a 200 mm. tube a reading of  $[\alpha] = -0.01^\circ$  was recorded. In another case the undissolved lime was washed three times with 5 c.c. of distilled water before dissolving in hydrochloric acid; the solution was optically inactive.

In order to determine the quantity of morphine retained in the mother liquor, after its precipitation from a lime solution by ammonium chloride, three experiments were carried out: (a) substituting 1 gm. of pure morphine only in the place of opium powder, as in B.P. 1898 process; (b) 1 gm. of pure morphine and 9.1 grms. of caustic potash; (c) 6.8 grms. of caustic soda in the places of opium powder and lime respectively. The morphine was precipitated by the usual process of adding ether, alcohol, and ammonium chloride. The mother liquors were evaporated to a small bulk to eliminate ammonia, ether, and alcohol, then acidified with dilute hydrochloric acid, made up to 104 c.c., and read in a 200 mm. tube.

Alkali Used.	Pure Morphine obtained (after Titration).	$[\alpha]$	Morphine left in Mother Liquor.
Calcium hydroxide ... ..	0.94	-0.51	0.0718 gm.
Sodium hydroxide ... ..	0.92	-0.76	0.1071 gm.
Potassium hydroxide ... ..	0.93	-0.71	0.1000 gm.

In the case of opium considerable difficulty was experienced in examining the mother liquor from the B.P. process, as it contained other active alkaloids which cannot be easily removed by extraction with solvents from the ammoniacal solution. They were, however, completely removed by extracting the lime solution with benzene, toluene, or ether. Annett and Singh (ANALYST, 1918, 43, 205) suggested

extraction of the lime solution of opium, before precipitation of morphine, by ether or toluene; but the 10 per cent. change in volume that would take place in the case with ether was overlooked. Solutions were prepared with water saturated with ether, and with ether saturated with water. After precipitation of morphine (B.P. 1898 process) the mother liquor was evaporated to a small bulk, acidified with hydrochloric acid, made up to 104 c.c., decolourised with 10 grms. of animal charcoal, and polarised in a 200 mm. tube.

Source of Opium.	Solvent used for Extraction.	$[\alpha]$	Total Morphine in 104 c.c.
Ghazipur ... ..	Benzene	-1.5	0.2113 gm.
" ... ..	Toluene	-1.4	0.1972 gm.
" ... ..	Ether	-1.5	0.2113 gm.
Lucknow ... ..	Toluene	-1.2	0.1690 gm.
Gwalior ... ..	Toluene	-1.2	0.1690 gm.
Cawnpur ... ..	Toluene	-1.4	0.1972 gm.

This proves indirectly that the allowance at present made for the retention of morphine in the mother liquor is incorrect so far as Indian opium is concerned. The figure obtained in the above experiment for the retained morphine in the mother liquor fairly represents the truth, since the solvents used for extraction dissolve most of the other active alkaloids of opium from its lime solution.

Source of Opium.	Process.	Total Crude Morphine per Cent.	Specific Rotation.
Morphine ... ..	—	—	-127.0°
Ghazipur ... ..	B.P. 1898	11.8	-124.1°
Ghazipur ... ..	B.P. 1914	11.7	-124.6°
Ghazipur ... ..	B.P. 1898 (after ether extraction of lime solution)	11.9	-122.7°
Ghazipur ... ..	B.P. 1898 (after toluene extraction of lime solution)	12.3	-118.6°
Etah ... ..	B.P. 1898 (after toluene extraction of lime solution)	11.4	-116.4°
Etah ... ..	B.P. 1898	10.9	-123.0°

The B.P. 1898 method estimates morphine in the crude morphine obtained in the process by titration with  $\frac{N}{10}$  sulphuric acid, using litmus as indicator, whilst in the 1914 method solution is effected in excess of the acid, followed by titration with  $\frac{N}{10}$  caustic soda, using methyl orange as indicator. It was thought that in these cases the neutralisation of acid might not be entirely due to morphine. It has been found that by using litmus as indicator less acid is consumed, which is there-

fore more correct, because any contamination of the crude morphine with narcotine, narceine, and papaverine is not indicated by litmus. To ascertain whether titration with acid is a true indication of morphine, 0.5 gm. of morphine was titrated in the above manner, made up to 50 c.c., and polarised in a 200 cm. tube. The specific rotation for morphine was calculated, taking the concentration to be what was found by titration :

It is thus seen that the morphine value based on titration does not necessarily indicate the actual truth, and the higher value obtained by the toluene extraction before precipitation of the alkaloid may be due to the contamination with a base or bases other than morphine. The 50 c.c. of ether (B.P. 1898 process) has been replaced by several other solvents; taking six portions of 1.4 gm. of pure morphine in the place of opium powder, and treating in the usual manner, 600 c.c. of calcium morphinate solution were prepared; this volume was shaken in a bottle, and portions of 10½ c.c. were taken in five conical flasks, and 11 c.c. of ether, ethyl acetate, benzene, toluene, were respectively introduced. Finally, ammonium chloride was added, and the assay set aside for precipitation overnight. The B.P. procedure of removal of the immiscible solvent by the pipette is never complete. Hence the contents of all flasks were placed in different separating funnels, the aqueous liquids run into the respective flasks, and the solvents filtered through tared papers. The liquids in the flasks shaken first with 20 c.c. and then 10 c.c. of ether, were placed in the separator, the ether was separated as before, filtered through the same filter, and washed with morphinated water. This set of experiments was also repeated with 600 c.c. of lime solution of opium.

Solvents.	With Pure Morphine.		With Opium	
	Gross Weight of Morphine.	Corrected Weight of Morphine by B.P. Process.	Gross Weight of Morphine.	Corrected Weight of Morphine by B.P. Process.
	Grm.	Grms.	Grms.	Grms.
Ether ... ..	0.94	1.050	1.01	1.10
Ethyl acetate ...	0.89	1.000	—	—
Benzene ... ..	0.95	1.050	1.07	1.13
Toluene ... ..	0.95	1.050	1.08	1.14

Experiments have been made with various samples of opium on the lines described above, using 50 c.c. of benzene, toluene, and ether side by side, and it was always observed that the results of the former two agreed fairly well themselves, but were always higher than when ether was used.

The B.P. 1898 process allows 4 per cent. increase in volume due to the dissolution of extractives from opium; in 1914 this figure was reduced to 2 per cent. The value for Indian opium has been worked out on the assumption that the sp. gr. of lime solution is 1.020 and the percentage of dry solid matter 4.565.

Weight of 100 c.c. of the lime extract of opium = 102.00 grms.  
 ,, ,, dry solid matter present in 100 c.c. = 4.565 grms.  
 volatile aqueous and fluid matter = 97.435 grms.

The sp. gr. of the distillate of an aliquot portion of the lime solution of opium was found to be 0.9997 at  $\frac{26^{\circ} \text{C.}}{26^{\circ} \text{C.}}$ . Hence the above 97.435 grms. is equal to 97.46 c.c. The liquid is practically water containing only a small quantity of bases (cf. Rakshit, *Pharm. J.*, 1917, **101**, 255). If 97.46 c.c. of water become 100 c.c. by the dissolution of the extractives, then the volume of 100 c.c. of water under similar circumstances is 102.6 c.c. Similarly, the following typical samples have been worked out:

Sample.	Process.	Sp. Gr. of Lime Extract.	Dry Solid Matter per Cent.	Volume of 100 c.c. of Water.
Morphine ... ..	1898	1.006	1.205	100.6
Morphine ... ..	1914	1.007	1.202	100.5
Ghazipur opium ... ..	1898	1.020	4.565	102.6
Ghazipur ,, ... ..	1914	1.020	4.430	102.5
Badaun ,, ... ..	1898	1.023	4.580	102.3
Badaun ,, ... ..	1914	1.022	4.935	102.8
Gwalior ,, ... ..	1898	1.017	3.905	102.3
Gwalior ,, ... ..	1914	1.018	4.255	102.5
Hill ,, ... ..	1898	1.020	4.350	102.4
Hill ,, ... ..	1914	1.020	4.305	102.3

It is obvious that the B.P. 1914 procedure is more correct than that formulated in 1898.

It has been observed that the specific rotation of morphine in dilute hydrochloric acid solution saturated with ether is  $-122^{\circ}$  at  $25^{\circ} \text{C.}$  with white light, and it is correct to use this figure instead of  $-127^{\circ}$  when employing the method described by one of us (*ANALYST*, 1918, **43**, 321). The results obtained by the polarimetric process become higher than the B.P. process. The mean residual morphine in the mother liquor of the B.P. 1898 process has been found to be 0.180 gm. in twenty-four analyses, and if this figure, instead of 0.104, be added to the titrated morphine value, then the two sets of results agree.

Sample.	Polarimetric Process.	B.P. 1898 with 0.180 Correction.
1. Ghazipur opium ... ..	11.8	11.9
2. Lucknow ,, ... ..	10.4	10.2
3. Cawnpur ,, ... ..	9.3	9.4

Although the B.P. result with the new correction figures agrees with that of the polarimetric method, yet the latter may be considered the more reliable.

*Conclusions.*—(1) The correction made for the retention of morphine in the mother liquor of opium after its precipitation by the B.P. procedure is too small.

2. Anything that neutralises acid in the crude morphine is not pure morphine.

3. 102 c.c. is a more correct volume of lime solution of opium to represent 10 grms. of opium in B.P. process than 104 c.c.

## ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

## FOOD AND DRUGS ANALYSIS.

**Chemistry of Burgundy Mixtures.** R. L. Mond and C. Heberlein. (*J. Chem. Soc.*, 1919, 115, 908-922.)—Investigation of the composition of mixtures of sodium carbonate and copper sulphate, commonly known as "Burgundy mixtures," shows that the chemistry of these is much more complex than was previously suspected. On mixing copper sulphate with sodium carbonate solution three distinct copper compounds are formed—namely, insoluble hydrated basic copper carbonate (this constitutes the bulk of the precipitate), insoluble hydrated basic copper sulphate, and soluble basic copper sulphate. Complete conversion of copper sulphate into these compounds is obtained by treating 4 grms. of crystallised copper sulphate with 4.25 grms. of crystallised sodium carbonate, but there appears to be no well-defined copper compound, the composition altering according to the conditions of precipitation. All the compounds undergo rapid changes, the basic copper carbonate losing carbon dioxide and the dissolved basic copper sulphate becoming insoluble. On dissolving the above quantities of copper sulphate and sodium carbonate each in 200 c.c. of water at 15° C., and mixing the solutions, the basic copper carbonate obtained contains CuO and CO<sub>2</sub> in the ratio 2.2 : 1, the insoluble basic copper sulphate contains CuO and SO<sub>3</sub> in the ratio 15 : 1, and the soluble basic copper sulphate contains 9.6 per cent. of the copper present; 52.4 per cent. of the carbon dioxide in the sodium carbonate is evolved in the free state. At higher temperatures, more carbon dioxide is evolved, until on reaching the boiling-point all is expelled and black copper oxide results. The amount of basic copper sulphate formed decreases with the quantity of sodium carbonate used, and the free carbon dioxide acts as a solvent on the basic copper sulphate only, not on the basic copper carbonate. The maximum of soluble basic copper sulphate is obtained with a mixture of 4 grms. of copper sulphate with 4.45 grms. of sodium carbonate, the minimum with the same amount of copper sulphate and 7.38 grms. of sodium carbonate. The copper precipitate at 15° C. contains adsorbed sodium carbonate in the ratio CuO : Na<sub>2</sub>CO<sub>3</sub> = 74 : 1. The whole of the copper precipitate is at first colloidal, but changes gradually to the crystalline state. Normal sodium carbonate and glue prolong the colloidal condition, but free copper sulphate, sodium hydrogen carbonate, and carbon dioxide accelerate the change to the crystalline state. The dissolved basic copper sulphate is in the form of hydrosol. Changes in the sulphur content of the copper precipitate take place during the change of the colloid to the crystalloid, and the crystalline precipitate contains less carbon dioxide than does the colloid; the ratio of CuO : CO<sub>2</sub> in old crystalline precipitate is found to be 2.94 : 1 (*Cf. Pickering, ANALYST*, 1908, 33, 62.)

W. P. S.

**Improved Method for Estimation of Caffeine in Vegetable Material.** F. B. Power and V. K. Chesnut. (*J. Amer. Chem. Soc.*, 1919, 41, 1298-1306.)—The finely ground material (10 grms.) is extracted for eight hours in a Soxhlet

apparatus with hot alcohol. The alcoholic extract is added to a suspension of 10 grms. of heavy magnesium oxide (free from sodium carbonate) in 100 c.c. of water. The mixture is evaporated on the water-bath to a nearly dry mass, and is then mixed with enough hot alcohol to enable it to be brought on to a smooth filter, the contents of which are then washed with successive portions of hot water until about 250 c.c. of filtrate are obtained. To the filtrate, contained in a 1,000 c.c. flask, 20 c.c. of 10 per cent. sulphuric acid are added, a small funnel is placed in the neck of the flask, and the liquid kept boiling for an hour. This treatment hydrolyses saponin. When cool, the liquid is passed through a double moistened filter into a separator, washing with 0.5 per cent. sulphuric acid. The clear acid filtrate is shaken with six successive portions of chloroform of 25 c.c. each. The united chloroform extracts are brought into another dry separator and shaken with 5 c.c. of 1 per cent. potassium hydroxide to remove colouring matter. The chloroform extract is run off through a dry filter into a conical flask and followed by two successive portions of 10 c.c. chloroform used for washing the alkaline layer. The chloroform is distilled off on the water-bath, the residual caffeine brought by means of a little chloroform into a tared beaker and, after the solvent has been allowed to evaporate spontaneously, the caffeine is dried for an hour in the water-oven and weighed.

G. C. J.

**Candle-Nut Oil. Lespinasse.** (*Ann. Falsific.*, 1919, 12, 152-153.)—The seeds of the candle-nut tree, *Aleurites triloba*, yield 7 to 10 per cent. of a pale yellow drying oil, which is termed "bancul oil" in the islands of the Pacific. A violent purgative principle is contained in the seeds, but remains almost entirely in the press-cake. A sample of expressed oil had the following characters: Sp. gr. at 15° C., 0.927; acidity (as oleic acid), 0.7 per cent.; saponification value, 175; and iodine value, 137.

C. A. M.

**Studies in Synthetic Drug Analysis. VII. Estimation of Monobrominated Camphor in Migraine Tablets. W. O. Emery.** (*J. Ind. and Eng. Chem.*, 1919, 11, 756-757.)—Migraine tablets may contain, in addition to vehicular and more or less inert materials, drugs such as acetanilide, caffeine, monobromo-camphor, and sometimes salicylates and plant extractives. The monobromo-camphor may be estimated by reduction with metallic sodium acting on an aqueous alcoholic solution, but the manipulation is difficult and uncertain owing to the tendency of the sodium to float during the evolution of the hydrogen. This difficulty is overcome by employing sodium amalgam, and the reduction is effected easily and quantitatively. Twenty or more tablets are weighed and powdered, and a portion of the sample equivalent to not less than 0.1 or more than 0.2 gm. of the bromo-camphor reputed to be present is weighed out. The sample is dissolved in 20 c.c. of 96 per cent. alcohol and 10 c.c. of water, and transferred to a small round-bottomed flask containing 15 grms. of 1 per cent. sodium amalgam. The flask is connected with a reflux condenser and the mixture is gently boiled for not less than thirty minutes. After cooling slightly, the condenser tube is washed out first with 5 c.c. of alcohol and then with 5 c.c. of water, the washings being received in the flask. The flask is heated on the water-bath for another hour or until the evolution of hydrogen has

practically ceased. Toward the end of this operation the liquid is approximately neutralised with acetic acid. It is then transferred to a Squibb separating-funnel from which the mercury is withdrawn, and washed in another funnel. The aqueous solution is filtered and the filtrate acidified with 5 c.c. of nitric acid; the bromide is precipitated with silver nitrate and collected in a Gooch crucible in the usual manner. The estimation should be controlled by a blank experiment. The weight of silver bromide is multiplied by the factor 1.23 to obtain the quantity of monobromo-camphor in the sample.

J. F. B.

**French Maize Products.** C. Granvigne. (*Ann. Falsific.*, 1919, 12, 145-147.)—In Burgundy and Franche-Comté, products made from roasted green maize flour, boiled with the addition of milk, butter, and salt, and known as *gaudes*, are extensively used for food. The flour used for the purpose is finely bolted whole maize meal. Four samples of these *gaudes* had the following composition: Moisture, 8.81 to 10.39; total nitrogen, 1.54 to 1.67; soluble nitrogen, 0.105 to 0.138; and fat, 4.67 to 5.46 per cent. (with iodine value 94.1 to 109.1). The ratio of soluble to total nitrogen ranged from 12.0 to 14.7, which is much higher than in the case of ordinary maize flour, the ratio for which is about 5 to 6.

C. A. M.

### BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

**Estimation of Sugar in Blood.** H. MacLean. (*Biochem. J.*, 1919, 13, 135-147.)—The employment of picric acid colorimetrically for determining sugar in blood is unsatisfactory owing to the presence of creatinine and other interfering substances which may cause a result to be obtained as much as 50 per cent. too high. The author (*J. Physiol.*, 1916, 50, 168) described a method involving the reduction of copper, and in the present paper describes fully the modified method he now adopts, firstly when 1 c.c. of the blood is available, and, secondly, where the determination is made upon 0.2 c.c. of blood. Blood proteins must first be separated very completely, and, to effect this, the blood is heated in acid saline solution (sodium sulphate and glacial acetic acid) which removes the greater part of the protein by coagulation, any remaining traces being removed by the addition of a small amount of dialysed iron. The sugar is estimated in an aliquot part of the clear and cooled filtrate by boiling with an alkaline copper solution containing potassium iodide and iodate. After boiling, the solution, which now contains the reduced cuprous oxide in suspension, is cooled and treated with a slight excess of hydrochloric acid, which, interacting with the iodide and iodate, liberates iodine equivalent to the amount of iodate in the solution; at the same time the cuprous oxide is dissolved and cuprous chloride formed, which latter is prevented from oxidation by the fact that free iodine is present, with which it immediately reacts. The amount of sugar present in the solution is calculated from the amount of iodine used up as determined by titration with thiosulphate. Particular attention must be paid to the regulation of the flame used for boiling the mixture of sugar and alkaline copper solution, full details being given in the paper, together with tables showing the dextrose equivalents in terms of  $\frac{N}{100}$  (1 c.c. of blood) and  $\frac{N}{400}$  (0.2 c.c. of blood) sodium thiosulphate solution. With



pure dextrose solutions theoretical results are obtained, and with blood, duplicates always agreeing within very narrow limits: In all blood-sugar estimations it is important to remember that glycolysis is often very active for a short time after the blood is drawn; all specimens should therefore be immediately measured, added to the coagulating mixture and heated at once in order to prevent such glycolysis, as standing for two hours at room temperature may reduce the amount of sugar present in the blood to less than half its original content. The following solutions are required. (A) Solutions for removing proteins from blood: (i.) Sodium sulphate 150 grms., glacial acetic acid 3 c.c., distilled water to 1000 c.c. This should be filtered through a starch-free filter paper. (ii.) Dialysed iron solution: this solution should be about B.P. strength and well dialysed; most samples on the market are practically not dialysed at all and contain large amounts of chlorides. (B) Solutions for estimating sugars in filtrate: (iii.) Alkaline copper iodide solution: Potassium bicarbonate 20 grms., potassium carbonate (anhydrous) 15 grms., copper sulphate crystals 0.7 grm., potassium iodate 0.11 grm., potassium iodide 1 grm., distilled water to 100 c.c. When dissolving the potassium bicarbonate the temperature must not rise above 37° C.; this is done first in 60-70 c.c. distilled water, and the potassium carbonate is then added. The copper sulphate is dissolved separately in a few c.c. of water and added to the mixed carbonates without waiting for the potassium carbonate to dissolve completely. After the resulting effervescence has passed, the complete solution of any remaining carbonate is effected by heating; the iodate and iodide are next added, the solution shaken and made up to 100 c.c. After filtering through starch-free paper it is ready for use and keeps indefinitely. The copper sulphate and potassium iodate must be weighed with great care. The solution must be standardised as regards its iodine content by taking exactly 3 c.c. of the mixture and adding this to 10 c.c. of the 15 per cent. sodium sulphate acetic acid used for deproteinising the blood; to this mixture 10 c.c. of 20 per cent. hydrochloric acid are added, the mixture very gently agitated until effervescence passes over and more strongly shaken for one minute; it is then titrated with  $\frac{N}{100}$  thiosulphate. The number of c.c. of thiosulphate used up gives the equivalent of iodine liberated from the mixture, and this should be recorded on the bottle. For 3 c.c. copper iodide solution about 8.8 c.c. of  $\frac{N}{100}$  thiosulphate are required, the exact figure depending upon the purity of the samples of iodate and iodide used. (iv.)  $\frac{N}{10}$  thiosulphate solution: This is prepared and standardised against  $\frac{N}{10}$  potassium bichromate; it is then diluted just before use either to  $\frac{N}{100}$  or  $\frac{N}{400}$  as required. (v.) Starch solution: Prepared in the ordinary way. (vi.) 20 per cent. hydrochloric acid solution: This is prepared by diluting 20 c.c. concentrated hydrochloric acid (sp. gr., 1.16) with distilled water to 100 c.c. The standardisation of the heating is effected by interposing a small manometer between the gas tap and the burner; a simple one may be extemporised by means of a T-piece and a piece of glass tubing bent in the form of a double-U and filled with a suitable liquid; by means of a screw clip the supply of gas may then be regulated so as to obtain the same pressure every time the flame is used, and when a strength of flame is found that brings the mixture to distinct boiling in about 1 minute 40 seconds the position of the fluid in both limbs of the manometer is marked. The original paper should be consulted for further details describing the technique of the

procedure adopted. In determining the sugar both in 1 c.c. and 0.2 c.c. of blood results of duplicate experiments are recorded showing an agreement within three units in the third decimal place per cent.

H. F. E. H.

**Picric Acid Method for the Estimation of Sugar in Blood.** O. L. V. de Wesselow. (*Biochem. J.*, 1919, **13**, 148-152.)—The colorimetric method for the estimation of sugar in blood by the use of picric acid as originally introduced by Lewis and Benedict (*J. Biol. Chem.*, 1915, **20**, 61), was modified by Benedict (*ibid.*, 1918, **34**, 203) and considerably simplified. Addis and Shevky (*ibid.*, 1918, **35**, 433) pointed out that the colour produced by the picric sugar reaction is not strictly proportional in intensity to the amount of sugar present; this the present author confirms. He finds that the sugar content of the whole blood as estimated by the Benedict method is always considerably higher than the results given by the method of MacLean (see preceding abstract), the excess averaging about 45 per cent. of the sugar present, whereas the Benedict results for blood plasma approximate closely to those obtained by the MacLean method, the excess amounting on an average to about 12 per cent. By the MacLean method the whole blood shows a slightly lower sugar content than the plasma, whereas the Benedict estimation shows a very considerable excess of sugar in the whole blood as compared with the plasma. All the results obtained appear to suggest the presence of an interfering substance in the corpuscles giving a colour reaction with picric acid, and thus raising the apparent sugar content of the whole blood. Creatinine estimations by the Folin method present an analogous case. (Hunter and Campbell, *ibid.*, 1917, **32**, 195.) This interfering substance reacts with the picric solution at an early stage of the heating, and is present to some slight extent in the plasma also, and, on account of its presence, the accurate estimation of sugar in whole blood by the picric acid method as described by Benedict is impossible.

H. F. E. H.

**Peroxydases in Milk.** H. Violle. (*Comptes rend.*, 1919, **169**, 248-250.)—Normal milk contains but little, if any, peroxydase; the latter is contained in the cellular tissue of the mammary glands, and in healthy animals the secretion of the peroxydase is very small. Any disease of the udder promotes increased secretion from the glands, and, consequently, milk from unsound animals contains larger amounts of the peroxydase. Although the peroxydase is destroyed when milk is heated at 78° to 80° C., it is quite easy to cause boiled milk to yield a positive reaction with any of the tests which have been proposed for the detection of peroxydase; potatoes, soya bean meal, green vegetables, etc., contain large quantities of peroxydase, and the addition of a small amount of any of these to boiled milk will make the latter yield a reaction for peroxydase, and thus be mistaken for unboiled milk.

W. P. S.

**Preparation of Silica Jelly for Use as a Bacteriological Medium.** A. T. Legg. (*Biochem. J.*, 1919, **13**, 107-110.)—The preparation of silica jelly according to published methods proved unsatisfactory, and it was found that the critical stages occurred during dialysis, for which purpose only membranes having a

permeability varying within certain limits were suitable. Brown (*Biochem. J.*, 1915, 9, 591) used prepared collodion membranes whose preparation involved the use of alcohol; this the author finds to be unnecessary and he employs a solution made up by dissolving 6 grms. of clean white guncotton in 100 c.c. of a mixture of equal parts of absolute alcohol and ether; 500 c.c. of this is made up at a time, allowed to stand for twenty-four hours and then decanted. It is impracticable to prepare the collodion solution of definite composition, but it should have a consistency similar to that of a heavy oil. Perfectly clean test-tubes,  $7\frac{1}{2}$  by  $1\frac{1}{2}$  inches, are coated internally with the collodion while revolved in a slanting position in the hand, after which the test-tube is filled with water for a few minutes, and the membrane is then detached with the aid of a needle, and removed by allowing water to pass between it and the glass. Membranes so prepared are slightly milky in appearance and are sufficiently strong for easy manipulation, they must be kept under water and never allowed to become dry. For the dialysis of silicic acid a membrane of this size, when filled with distilled water and suspended in air, should not allow the water to drop oftener than once in twelve seconds; membranes are more reliable when fairly thick, and may be used many times. Pure re-fused sodium silicate was used for the preparation of nitrogen-free media. This is supplied in opaque lumps which are slowly soluble in boiling water, but are readily brought into solution when raised to a temperature of  $140^{\circ}$  C. for one hour in the autoclave. One hundred grms. of sodium silicate in a litre of distilled water are readily diluted to give a solution of sp. gr. 1.09. Equal volumes of hydrochloric acid (sp. gr. 1.10) and silicate solutions are taken, the former is poured into a conical flask and the latter into a large separating funnel and dropped into the acid which is shaken meanwhile. This acid mixture is allowed to stand from three to four hours, according to the temperature of the laboratory, in order that the necessary chemical reaction may take place, the longer period being given when the temperature is below  $15^{\circ}$  C. The mixture is then poured into a separating funnel and thence into the membrane, which is supported in a vessel of water to avoid undue strain. When nearly full, the neck of the membrane is drawn together and secured with a rubber band, and the membrane suspended in a gas cylinder—or other suitable vessel—of distilled water to dialyse. The distilled water is changed hourly during the day and dialysis continued until the silicic acid is neutral to litmus. Running tap-water as supplied to the town of Reading was repeatedly tried for dialysis, but always caused the silicic acid to get into the membrane before dialysis was complete. When neutral to litmus, the silicic acid is poured into a beaker, the nutrient salts added in concentrated solution, and the medium boiled for five minutes to expel air. If not sufficiently boiled the plugs will be blown out of the tubes in the autoclave and an uneven gel will result. The medium is “tubed” whilst hot, and immediately autoclaved for twenty minutes at from  $135$ - $140^{\circ}$  C. Silicic acid prepared in this way forms a gel on autoclaving; if slants are required the tubes must be placed in the requisite positions in the autoclave, as the gel once formed is irreversible. The success of the process depends upon: (1) The use of a membrane of standard permeability; a rather thick membrane of low permeability gives the best results. (2) A sufficiently long period being given for the sodium silicate and hydrochloric acid to react after mixing; this is a critical factor. (3) The use of distilled water for

dialysing; constant changes of water especially in the earlier stages of dialysis in a vessel just large enough to take a membrane are best. (4) Tubing the medium as quickly as possible after removal from the membrane and immediate autoclaving. The autoclave should be heated up while the medium is being tubed. It is advisable, owing to the action of silicon compounds on glass, to restrict the use of glass apparatus so far as possible during the preparation of the jelly. H. F. E. H.

### ORGANIC ANALYSIS.

**Estimation of Acetylene in Presence of Ethylene.** W. H. Ross and H. L. Trumbull. (*J. Amer. Chem. Soc.*, 1919, **41**, 1180-1189.)—The method described is a modification of that of Chavastelon (*Comptes rend.*, 1897, **125**, 245) who absorbed acetylene in excess of neutral silver nitrate solution and titrated the liberated nitric acid with sodium hydroxide in presence of phenolphthalein. In the original method the end-point is somewhat masked by the brown colour of silver oxide. Addition of sodium chloride to precipitate excess silver before adding the alkali does not improve matters, but if alkali be added in slight excess until the brown colour of silver oxide appears, and then sodium chloride to precipitate silver, the excess of alkali can be titrated to a sharp end-point. But, although the end-point is sharp, the results are not exact, as phenolphthalein is not a suitable indicator. Substituting for it methyl orange, exact results are obtained.

The authors collect their samples in a gas burette over mercury, and carry out the absorption in a specially designed pipette containing a 2.5 per cent. solution of silver nitrate. The pipette is constructed from a flask, a two-hole rubber stopper, and a 50 c.c. bulb-tube, open at both ends, one end being provided with a stopcock, and the other passing through the rubber stopper to the bottom of the flask. Into the flask about 100 c.c. of silver nitrate solution are introduced and this is sucked up into the bulb until it is full, when the stopcock is closed. Connection is then made with the burette and a measured volume of gas passed into the bulb, the stopcock of which is then closed. The pipette is disconnected from the burette and shaken until absorption is complete, when the contents of the bulb are washed into the flask and titrated as described. The method is not only rapid, accurate, and simple, but has the advantage of giving accurate results in presence of such gases as vinyl bromide, which is readily absorbed by bromine, fuming sulphuric acid, or neutral or ammoniacal silver nitrate. G. C. J.

**Critical Temperature of Solution of Hydrocarbons in Aniline. Application to the Analysis of Petroleum Spirit.** C. Chavanne and L. J. Simon. (*Comptes rend.*, 1919, **169**, 185-188.)—The authors have previously recorded the critical temperatures of solution in aniline of the principal volatile hydrocarbons (B.P. under 150° C.) contained in petroleum spirit (*Comptes rend.*, 1919, **168**, 1111.) In conjunction with a fractional distillation it is possible from these values to obtain a method for the analysis of petroleum spirit. The critical temperature of solution of acyclic hydrocarbons lies between 69° and 74° C.; that of saturated cyclic hydrocarbons between 18° and 49° C., whilst aromatic hydrocarbons are miscible in all proportions

with aniline. To determine aromatic hydrocarbons in petroleum spirit, B.P. below 150° C., the sample is fractionally distilled, and the critical temperature of solution is determined for each fraction: the aromatic hydrocarbon is then eliminated by nitration, the determination is repeated (for each fraction), the rise in the value being a measure of the benzene present. Toluene and xylene are estimated in a similar way. Saturated cyclic hydrocarbons may be estimated by removing the aromatic hydrocarbons by nitration, and then submitting the sample to fractional distillation, so that each fraction consists of a cyclic hydrocarbon mixed with one or two acyclic hydrocarbons; the critical temperature of solution is determined for these fractions and the amount of cyclic hydrocarbon present calculated from the sum of the values obtained.

W. P. S.

**Estimation of Aniline in Dilute Aqueous Solution.** W. G. O. Christiansen. (*J. Ind. and Eng. Chem.*, 1919, 11, 763-764.)—For the estimation of aniline in water from the rectification process, the author recommends the well-known hypochlorite reaction, and a series of standard colours made up to correspond to known concentrations of aniline. To 5 c.c. of aniline solution in a standard test-tube, 1 drop of dilute sodium hydroxide solution is added, then 3 drops of a saturated aqueous solution of phenol and 4 c.c. of freshly prepared saturated solution of bleaching-powder. After standing for half-an-hour the liquid is diluted with 50 c.c. of water and compared with the standard colour solutions in test-tubes of identical size, in front of an electric light. The colorimeter is made by cutting two slits  $\frac{1}{4}$  in.  $\times$  2 ins. in a sheet of thick cardboard, the slits being 1 in. apart. Above each of the slits a loop of wire is arranged to support a test-tube 16  $\times$  120 mm. containing the solutions. The standard colour solutions are prepared by matching solutions of known quantities of aniline ranging from 0.1 to 0.5 per cent. against mixtures of diluted blue and red inks, the solutions being dulled to the right degree of opacity by the addition of powdered calcium carbonate. With these permanent standards the method of analysing the rectification waters is very rapid, and a dozen samples can be dealt with in an hour with an accuracy quite sufficient for plant control.

J. F. B.

**Cuprous Chloride—Iodine Method for Reducing Sugars Simplified.** F. M. Scales. (*J. Ind. and Eng. Chem.*, 1919, 11, 747-750.)—The iodine method for estimating the cuprous oxide after conversion into chloride has been further investigated with a view to its simplification. Cammidge's recommendation to use Benedict's copper solution has been adopted owing to the protective advantage derived from the generation of carbon dioxide on acidification. Benedict's solution is made up as follows: Copper sulphate crystals, 16.0 grms.; sodium citrate, 150 grms.; dry sodium carbonate, 130 grms.; sodium bicarbonate, 10 grms., diluted to 1 litre. The other reagents comprise  $\frac{N}{25}$ -solutions of iodine and thiosulphate, dilute hydrochloric acid containing 1.5 c.c. of concentrated acid per 25 c.c., and dilute acetic acid containing 2.4 c.c. of glacial acid per 100 c.c. Twenty c.c. of Benedict's solution are placed in a 300 c.c. conical flask and the volume is made up to 30 c.c. with the sugar solution and water. If more than 20 mgrms. of dextrose be present 25 c.c. of Benedict's solution should be taken and a total volume of 35 c.c. The

flask is heated either by a flame or hot plate so that the liquid boils in four minutes in the former case, or five minutes in the latter. The period of heating and intensity of the heat must always be constant; boiling is continued for three minutes. The flask is quickly cooled under the tap. When cold, 100 c.c. of dilute acetic acid are added and iodine is immediately run in from a burette. Twenty-five c.c. of dilute hydrochloric acid are discharged from a pipette all round the walls of the flask and the liquid is vigorously rotated at the same time. The pipette and sides of the flask are washed down with a little water and the solution is rotated for one minute; any precipitate should be dissolved in that time. The excess of iodine is then titrated with the thiosulphate; this excess should be arranged to be equivalent to between 5 and 8 c.c. of the thiosulphate. The control of the estimation depends very greatly on the uniformity of the conditions of heating, and if this be ensured the dextrose equivalent of the thiosulphate solution is practically constant and independent of the quantity of dextrose between the limits 1.5 to 24.0 mgrms. of dextrose which were investigated by the author; duplicate estimations differ by less than 0.1 mgrm. of dextrose.

J. F. B.

**Paint Analysis. G. J. Hough.** (*J. Ind. and Eng. Chem.*, 1919, 11, 767-768.)—

1. *Estimation of Cuprous Copper in Copper Paints.*—Paints intended for the bottoms of ships are specified to contain a certain amount of copper in the form of cuprous oxide. In the case of ready mixed paints, the pigment must be freed from the oily vehicle and dried. Then 0.5 gm. of the pigment is treated with 10 c.c. of concentrated hydrochloric acid, the mixture is heated gently for several minutes to dissolve all the copper, diluted with cold water to about 200 c.c., treated with 5 c.c. of phosphoric acid, and at once titrated with permanganate. The results are good except when the sample contains much unextracted matter, which introduces a slight error. The permanganate may be standardised against carefully purified cuprous oxide, but when standardised against iron the factor 1.166 is used instead of the theoretical factor 1.125 in converting the iron value into copper value.

2. *Rapid Method for the Estimation of Lime in White Lead.*—In many cases, such as putty, white lead is mixed with lime in the form of calcium carbonate; the white lead is extracted from the mixed pigments by hot dilute caustic soda solution. From 0.5 to 1.0 gm. of the pigment is boiled for several minutes with 50 c.c. of 5 per cent. sodium hydroxide solution. The liquid is decanted through a filter, a little more caustic soda is added, then hot water, and the liquid again decanted. The residue is washed well by decantation with hot water, and the filter is washed four times. The residue is dissolved in hot hydrochloric acid, the solution neutralised by ammonia, any lead precipitate is filtered off and the calcium is precipitated as oxalate. If the pigment contain more than 50 per cent. of white lead the boiling with caustic soda should be repeated a second or even a third time.

3. *Chromium in Mixed Pigments.*—For the detection of small quantities of chromium in mixed pigments, the material is treated with dilute nitric acid (1 to 5), stirred, allowed to stand for a few minutes, and then filtered; the filtrate is treated with a few c.c. of hydrogen peroxide. A purple colour indicates chromium, the

chromic acid being oxidised to perchromic acid. To be successful, the chromium must be present as chromic acid, and the solution must not be heated.

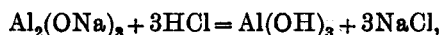
4. *Estimation of Chromium in Chrome Yellow.*—About 0.5 gm. of the pigment is treated with 15 c.c. of 20 per cent. sodium hydroxide and warmed until dissolved. The solution is diluted to about 200 c.c. with cold water, 2 grms. of ferrous ammonium sulphate dissolved in a little water are added; the mixture is stirred, allowed to stand for a few minutes, then strongly acidified with dilute sulphuric acid, diluted when cold to nearly 400 c.c. and titrated with permanganate or potassium dichromate. This method is better than the old method in which the chromate is dissolved in hydrochloric acid, as some samples of chrome yellow are partially insoluble in acid.

5. *Preparation of Starch Indicator.*—A permanent solution of starch which is clear, transparent, and gives a fine blue colour with iodine is prepared by dissolving 1 gm. of salicylic acid in 100 c.c. of water, boiling, adding this to 1 gm. of potato starch mixed with a little water, boiling the mixture until the starch is dissolved, cooling slightly and diluting with cold water to 1 litre. This indicator may be preserved indefinitely.

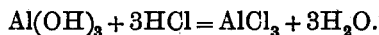
J. F. B.

### INORGANIC ANALYSIS.

**Alkalimetric Titration in Presence of Alumina.** J. Bellucci and F. Lucchesi. (*Annali. Chim. applic.*, 1919, 11, 199-204.)—In titrating sodium aluminate with hydrochloric acid, using phenolphthalein as indicator, the following reaction takes place :



whilst on titrating aluminium hydroxide, using methyl orange as indicator, the reaction is :



In titrating crude alkalis containing only negligible amounts of alumina, methyl orange may be used as indicator, but should any material proportion of aluminium be present, the alkaline solution is boiled for five minutes with a slight excess (1 to 2 c.c.) of  $\frac{N}{1}$ -acid, in presence of phenolphthalein, cooled to the ordinary temperature, and titrated back with  $\frac{N}{1}$ -alkali. In titrating sodium hydroxide in sodium aluminate, Lunge's method (*Zeitsch. angew. Chem.*, 1890, 227, 293) may be used, according to which the sample is dissolved in water and an aliquot portion titrated with  $\frac{N}{2}$  hydrochloric acid in presence of phenolphthalein. But if, as directed, the titration is effected in the boiling liquid as a safeguard against carbon dioxide, the results will be too low. For example, 10 c.c. of a solution containing 0.2 gm. of sodium aluminate required 10.2 c.c. of  $\frac{N}{2}$  hydrochloric acid at boiling-point, and 11.1 c.c. at the ordinary temperature. It is therefore necessary to titrate the boiling liquid until colourless, then to cool the flask rapidly in a current of cold water, and to complete the titration of the cold liquid.

C. A. M.

**Analytical Method for Determining Efficiency of Ammonia Oxidation.** D. P. Gaillard. (*J. Ind. and Eng. Chem.*, 1919, 11, 745-747.)—The control of plant in which ammonia is being oxidised to oxides of nitrogen is best performed by

making frequent analyses of the gases entering and leaving the conversion chamber, the components being determined as percentages by weight. For this purpose samples are collected in previously weighed evacuated bulbs of 500 to 600 c.c. capacity, the weight of the sample is then determined, and the contents of the bulb are absorbed in standard acid and alkali. The bulbs, with well greased stopcocks, are evacuated to a pressure of about 2 cm. of mercury, weighed, and tested for leakage. The stem of the bulb is then connected by a rubber sleeve to short glass sampling tubes extending into the path of the gases through a hole in a well-fitting cork inserted in the side of the conversion chamber. After a uniform temperature has been established, the stopcocks of the bulbs at [the entrance and exit points of the chamber are quickly opened wide, and again closed in order to take the samples, and the bulbs are again weighed. In the case of the entrance sample the tube of the bulb is dipped in water and the water allowed to rise into the bulb as far as possible. The contents of the bulb are shaken to absorb the ammonia, and air is then blown into the bulb. This enables the ammoniacal water to be discharged into 25 c.c. of  $\frac{N}{10}$  sulphuric acid. The bulb is washed out with water three times, the water being introduced into the bulb by suction. The excess of acid is titrated, using methyl-red as indicator. In the case of the exit sample, about 100 c.c. of water are first admitted without allowing air to enter. About 25 c.c. of oxygen are then admitted from a small container, and the contents of the bulb well shaken and allowed to stand for a minute. The residual vacuum is destroyed, and the bulb is again shaken for five minutes. The contents and washings are discharged into 15 c.c. of  $\frac{N}{10}$  sodium hydroxide and the excess of alkali is titrated, using methyl-red as indicator. Slight sources of error are introduced by the dilution of the sample with the air drawn from the sample tube into the bulb ahead of the sample. Other sources of error, which can be practically eliminated by care in manipulation, are condensation in the sample tube when taking the sample, leakage of air into the converter around the sampling hole when the vacuum is suddenly applied, changes in temperature, pressure and moisture conditions between successive weighings of the same bulb, and incomplete absorption of the gases in the bulb. Any small amount of ammonia remaining unoxidised in the exit gases also introduces an error which is generally negligible. On the whole, the precision of the method is believed to lie between plus and minus 0.75 per cent. A succession of instantaneous samples taken in this way at frequent intervals has been found to give more reliable operating details than a continuous sample taken over the same period. J. F. B.

**New Method of Chemical Analysis.** A. W. Hull. (*J. Amer. Chem. Soc.*, 1919, 41, 1168-1175.)—The method described is a method of X-ray analysis, fundamentally different from X-ray spectrum analysis, and from what may be called the X-ray absorption band method. It is simpler than these methods in that it does not require a spectrometer, and it supplements them in that it gives evidence which they do not supply—namely, the state of chemical combination for each of the elements present. It consists in reducing to powder form about 1 cub. mm. of the substance to be examined, placing it in a small glass tube, sending a beam of monochromatic X rays through it, and photographing the diffraction pattern produced. The only apparatus



required is a source of voltage, an X-ray tube, and a photographic film. The method is applicable to all chemical elements and compounds which are crystalline. The rays from the X-ray tube pass first through a sheet of metal, properly chosen, serving as a filter. The filter is chosen of such material that it specially absorbs all wave lengths shorter than the desired one, leaving practically nothing but a single intense line, the  $\alpha$  line of the K series of the anode material. For a molybdenum X-ray tube the proper material is zirconium. The rays then pass through slits in two thin sheets of lead, some little distance apart. This confines the rays to a narrow beam about 1 mm. wide. Next comes the thin-walled glass, celluloid or collodion tube containing the substance to be tested. Beyond this, and with this as its centre, is a semi-circular strip of brass to which is attached a strip of photographic film. An exposure of an hour generally gives all the information desired. When the film is developed it shows, in addition to the over-exposed line in the centre, where the direct beam strikes, a series of other lines on each side of the centre. These lines are caused by the "reflections" of the X rays from the tiny crystals in the powder. Their distance from the centre of the film depends on the distance between the planes of atoms in the crystal, and there is one line for every important set of planes in the crystal. It is evident, therefore, that substances with different crystalline structure will give entirely different patterns of lines. Substances of similar chemical nature, on the other hand, will in general have similar crystal structure and give similar patterns, one being simply a magnified image of the other. The magnification or spread of the pattern is different for each one, being inversely proportional to the cube root of the molecular volume. Since no two substances have exactly the same molecular volume, it is easy to distinguish them, as the difference is cumulative for lines far from the centre. Photographs are given in the paper showing how, for instance, a mixture of sodium fluoride and potassium chloride can be recognised as such, and readily distinguished from a mixture of sodium chloride and potassium fluoride. The method is further capable of quantitative application.

G. C. J.

**Adaptation of the Mohr Volumetric Method to General Determinations of Chlorine.** L. Yoder. (*J. Ind. and Eng. Chem.*, 1919, 11, 755.)—The conditions necessary for the accurate titration of chlorides with potassium chromate as indicator are that the solution be neutral; that no carbonates or phosphates be present, since the silver salts of these acids are less soluble than the red silver chromate; that the solution of the chlorides must have a proper concentration to produce the most definite colour change. The author has worked out a method which is designed to give titratable solutions in the case of organic materials containing only small quantities of chlorine. The material is thoroughly saturated with water containing 5 c.c. of a 30 per cent. solution of calcium acetate. The mixture is evaporated to dryness at 120° C. and ignited at a temperature not exceeding 450° C. The cooled residue is thoroughly moistened with a few c.c. of a 10 per cent. solution of ferric acetate, and again evaporated to dryness and ignited not above 450° C. The residue is triturated with hot water, filtered and washed until free from chlorides. The filtrate is evaporated to dryness or nearly so, and the residue is taken up with just sufficient hot water to ensure complete solution of the chlorides, when cold. After

the addition of 2 or 3 drops of potassium chromate, the solution is titrated with  $\frac{N}{20}$  silver nitrate. The calcium acetate fixes free chlorine, and during the extraction of the ignited residue precipitates carbonates, and neutralises the filtrate. The ferric acetate precipitates the phosphates and is itself converted into the insoluble oxide which is removed by the filtration. The method has been shown to give good results as compared with the gravimetric method when applied to materials such as fæces, grain, hay, etc.

J. F. B.

**Acid Test on Enamel Ware.** W. D. Collins. (*J. Ind. and Eng. Chem.*, 1919, 11, 757-759.)—The test by boiling with 4 per cent. acetic acid may be considered fairly representative, as regards antimony, of the action of certain foodstuffs on enamelled steel domestic utensils; in some cases the test is made with 1 per cent. tartaric acid. The observations to be made at the end of the test relate to: (1) *Appearance*.—The extent to which the glaze is attacked is noted, and the results grouped into three classes—good, fair, and bad; “good” represents only a slight dulling of the glaze, and “bad” indicates its almost complete disappearance. Blue ware showed the highest percentage of “bad,” and white ware of “good.” (2) *Loss of weight*.—This item is not of very characteristic value. Certain tests made by boiling for six hours with 200 c.c. of 4 per cent. acetic acid, and evaporating the solution, showed soluble matter from 0.05 to 0.08 grm. for “good” pans, and up to 0.6 to 1.2 grms. for “bad” ones. (3) *Silica in the dissolved matter*. (4) *Antimony*.—The acid solutions, after boiling for half an hour, are treated with hydrogen sulphide. The antimony sulphide is dissolved in boiling concentrated hydrochloric acid. The solution is filtered, diluted, treated with starch and iodine to oxidise any reduced tin, made alkaline with sodium carbonate, acidified with tartaric acid, and then made alkaline with sodium bicarbonate. The antimony is titrated with iodine solution such that 1 c.c. is equivalent to 0.606 mgrm. of antimony. Tartaric acid dissolves more antimony than acetic acid. White and grey ware frequently contain antimony, but can be obtained without it; blue ware is generally free from antimony. (5) *Lead*.—The ware of most manufacturers was found to be free from lead; in one case acetic acid dissolved from 2 to 9 mgrms. of lead. (6) *Chipping with changes of temperature*.—A number of the samples examined were not satisfactory in this respect, the tests being no more severe than the treatment in ordinary use. In some cases the enamel chipped as soon as the flame was applied, and occasionally after removing from the flame to a tile at the ordinary temperature.

J. F. B.

**Action of Water and Hydrochloric Acid on Powdered Glass.** P. Nicolardot. (*Comptes rend.*, 1919, 169, 335-337.)—It has been proposed to determine the solvent action of solutions on glass by placing the solvent in contact with the powdered glass, and this method has been made official by the Physikalische Reichsanstalt; under these conditions the solvent action varies with the composition of the glass, and especially with the degree of fineness of the powder. The results given in the following table are expressed in parts per thousand, by weight; the powders were sifted into three grades, the particles having surfaces in the ratio

of 1 : 2.84 : 12.8, and each was boiled for three hours in platinum vessels with 300 c.c. of water or  $\frac{N}{10}$  hydrochloric acid, the final volume being 100 c.c. in each case.

## Action of Water.

	A.	B.	C.	Jena.	Thurin- gian.	Krasna.	Kavalier.	Zsolna.
Entire glass (conical flask) ...	0.12	0.11	0.11	0.09	0.03	0.44	0.28	0.12
Coarse powder ...	1.75	1.00	0.25	0.25	0.25	4.25	1.75	0.25
Medium powder ...	2.50	2.00	1.00	0.75	0.75	9.00	2.75	0.75
Fine powder ...	12.75	10.00	6.25	2.75	5.25	61.50	18.50	5.50

## Action of Hydrochloric Acid.

Entire glass ...	0.02	0.02	0.01	0.03	0.01	0.03	0.04	0.0
Coarse powder ...	0.50	0.25	1.00	2.00	0.75	2.00	0.75	1.0
Medium powder ...	3.50	1.75	2.25	5.25	3.75	6.25	2.50	3.5
Fine powder ...	32.25	17.00	16.50	40.25	12.50	49.00	17.00	12.0

If the losses in the medium and fine powders are divided by 2.84 and 12.8 respectively, to eliminate the effect of surface, it will be found that practically the same figures are obtained for the action of water, whilst in the case of hydrochloric acid the solvent power increases with the fineness of the powder. It will be noticed that, with Jena glass, hydrochloric acid dissolves more of the powders than does water, whilst the opposite effect is obtained with the entire glass. This would explain the fact that Jena glass is relatively more soluble in hydrochloric acid than are the French glasses, A, B, and C, after the glasses have been heated in an autoclave; the heating detaches particles of the Jena glass, and these dissolve in the acid.

W. P. S.

**Alkalimetric Determination of Small Amounts of Magnesium.** P. L. Hibbard. (*J. Ind. and Eng. Chem.*, 1919, 11, 753-754.)—The author has investigated the method devised by Brückmiller for the titration of ammonium magnesium phosphate, extending it to the estimation of small quantities of 5 mgrms. or less, such as have been estimated in soil extracts. The modifications comprise the use of the Gooch crucible for filtration, whereby washing can be done with the smallest quantity of liquid; the selection of a suitable washing medium consisting of neutralised alcohol followed by an aqueous solution of ammonium magnesium phosphate, and the use of methyl red as indicator. The use of alcohol for the removal of the excess of ammonia from the precipitate is necessary because the ammonia would precipitate phosphate from the saturated aqueous solution of the ammonium magnesium phosphate. If the alcohol be properly neutralised it has no appreciable solvent action. The solution containing the magnesium to be estimated should be free from other bases giving insoluble phosphates, the filtrate from the precipitation of calcium oxalate being preferably used. The volume should be small—namely, for amounts

less than 1 mgrm., 5 c.c.; for 1 to 3 mgrms., 10 c.c.; for 5 mgrms., 20 c.c. Other salts should be absent as far as possible, ammonium salts being removed by ignition. Precipitation of the phosphate may be performed either cold or hot. According to the former method the solution should contain 0.1 to 0.2 per cent. of ammonium chloride, and enough free ammonia to give a distinct but not strong odour. A 1.5 per cent. solution of sodium ammonium phosphate is added drop by drop, 1 c.c. per 1 mgrm. of magnesium. After ten minutes one-third volume of strong ammonia is added, and the precipitate is filtered after two hours or more. The hot method gives good results when excess of ammonium salts are present. The liquid is slightly acidified with hydrochloric acid, heated to boiling, treated with phosphate solution, then with one-third volume of strong ammonia, and allowed to stand for at least two hours and cool. In collecting the precipitate in the Gooch crucible a moderately thick layer of paper pulp should be used in preference to asbestos. The main portion of soluble salts may be washed out with 2 per cent. ammonia solution, or else alcohol may be used at once. The precipitate is washed three or four times with 95 per cent. alcohol neutralised in accordance with a separate titration in which the alcohol is diluted with water, and methyl red is used as indicator. After washing with alcohol, four washes of 5 c.c. each are given with a saturated aqueous solution of ammonium magnesium phosphate. The sides of the crucible are washed down, and the felt is removed with the precipitate, placed in the precipitation flask with water and methyl-red, and an excess of standard acid is run in while shaking. Sufficient time must be allowed for the precipitate to dissolve, and the excess of acid is titrated back. When more than 2 mgrms. of magnesium are present the colour change is not sharp.

J. F. B.

#### Colour Reaction for the Detection of Mercury in its Compounds.

**A. Abelmann.** (*Pharm. Zentralb.*, 1919, 60, 247-248.)—The following reaction is given by mercury salts and its compounds in general, and even by those organic mercury compounds in which the mercury is so firmly combined that it does not yield a coloration with hydrogen sulphide unless the compound is decomposed previously. A solution of the mercury salt or compound, or a suspension of an insoluble compound, is treated with a drop of dilute nitric acid and a moderate quantity of ferrous sulphate solution. Concentrated sulphuric acid is then added cautiously, so as to form a layer below the mixture. A red-violet ring appears at the junction of the two liquids and persists for some hours. The brown ring, due to the usual nitric acid-ferrous sulphate reaction, appears somewhat later, and is seen above the red-violet ring.

W. P. S.

**New Method of Analysing Platinum Ores and Chemical Composition of the Ural Ores.** **L. Duparc.** (*Helv. Chim. Acta*, 1919, 2, 324-337.)—The crude platinum ores of the Ural district are of complex composition. Apart from the natural alloy, which composes the mineral, small quantities of iridium osmide and palladium are invariably present, with granules of iron or ferro-nickel, and sometimes free iridium. The alloy itself consists of platinum associated with more or less iron (up to 20 per cent.), iridium, palladium, rhodium, and copper, and frequently

nickel. In practice the ores are classified into the ferro-platinum ores, which contain from 15 to 20 per cent. of iron, and the polyxenites, which contain only 6 to 10 per cent., the former being attracted by the magnet, whilst the latter are not. All the natural alloys of platinum enclose a variable quantity of crystals of iridium osmide, which remain intact after the mineral has been treated with *aqua regia*. The following method of analysing these types of ores has been devised:

*Estimation of Osmium and Silica*—About 10 grms. of the mineral are heated on the sand-bath at 80° C. with *aqua regia*, and the insoluble osmides and silica are separated, washed with hot water, ignited and weighed together. They are then fused with 5 to 6 grms. of finely-divided metallic silver and an excess of borax in a refractory earthenware crucible previously glazed with borax. The fused mass is treated with nitric acid, and the insoluble osmide separated, washed, ignited, and weighed, whilst the silica dissolved by the borax is found by difference.

*Precipitation of Iridium and Platinum*—The filtrate from the silica and osmium is repeatedly evaporated on the water-bath to expel nitrous products, the residue is dissolved in hot water, and the liquid oxidised for thirty minutes by means of a current of chlorine. It is then concentrated to a paste in an oven at 38° to 42° C., which temperature must not be exceeded, in order to prevent the reduction of gold and formation of basic salts, and to keep the iridium in the form of the tetrachloride. On now adding 25 to 30 grms. of ammonium chloride in successive small portions the whole of the platinum and iridium is precipitated as double salts. After standing for two days the precipitate is separated, and washed with a saturated solution of ammonium chloride (500 to 600 c.c.) until the filtrate ceases to give a reaction for iron with thiocyanate. The precipitate is then washed with a little alcohol, the alcoholic filtrate evaporated to dryness, the residue dissolved in water, and the solution added to the first filtrate and washings. The filter-paper and its contents are ignited in a muffle furnace, the residue treated with hydrochloric acid to remove the last traces of iron, then ignited in a current of hydrogen, cooled in carbon dioxide, and the iridium and platinum weighed together.

*Separation of Iridium and Platinum*—The residue is treated in a covered porcelain basin with *aqua regia* diluted with five times its volume of water at a temperature not exceeding 50° C. This operation is repeated with fresh quantities of acid until, after a digestion of 12 hours, nothing more dissolves. The residue is washed with 1 per cent. hydrochloric acid, washed on the filter with water, ignited in hydrogen, cooled in carbon dioxide, and weighed as iridium. The filtrate is again treated with ammonium chloride, and the platinum estimated in the usual way as platinochloride.

*Separation of Gold and Palladium*—The filtrate from the first precipitation with ammonium chloride is heated on the water-bath with a solution of 0.75 to 1 gm. of dimethylglyoxime in boiling water until a yellowish-brown precipitate is formed (or yellow in the absence of gold). This precipitate is washed with acidulated water, dried, and ignited in a tared porcelain crucible, after which it is redissolved in *aqua regia*, the nitric acid expelled by repeated evaporation with hydrochloric acid, and the residue taken up with water. The solution is treated with ammonium chloride, and any precipitate of platinum is added to that previously obtained. The filtrate from the platinum is evaporated to dryness, the residue

treated several times with strong nitric acid, and then with hydrochloric acid, and the solution again evaporated to dryness. The residue is dissolved in water, and treated at 60° C. with 2 grms. of ammonium oxalate which precipitates the gold quantitatively in four to six hours, and the precipitate is washed, dried, ignited and weighed as metallic gold. The filtrate is nearly neutralised with ammonia, treated with 1 gm. of dimethylglyoxime dissolved in boiling water, and the yellow precipitate is washed with acidulated water, dried, ignited in a current of hydrogen, cooled in a current of carbon dioxide, and weighed as metallic palladium. *Separation of Copper and Rhodium*—The filtrate from the gold and palladium is reduced for five to six hours by means of 50 grms. of pure zinc and 50 grms. of strong hydrochloric acid, the black deposit rapidly filtered off, washed until free from acid, and ignited in a tared porcelain crucible. The residue is triturated at intervals in a glass mortar with 50 per cent. nitric acid for about two hours, the clear liquid decanted, and the treatment with acid repeated. The residue will contain the rhodium (with sometimes a little platinum), whilst the filtrate will contain all the copper (with sometimes traces of rhodium). The filtrate is repeatedly evaporated to dryness with strong hydrochloric acid, the residue taken up with water, and the copper precipitated as thiocyanate in the usual way. The filtrate from the copper is evaporated to dryness, and the residue treated with ordinary nitric acid, next with concentrated nitric acid to decompose the thiocyanates, and is then taken up with water and reduced with zinc and hydrochloric acid. This throws down any traces of rhodium, and this precipitate is ignited and added to the original rhodium residue. This is fused for about thirty hours with potassium bisulphate, when the rhodium will be rendered soluble, whilst traces of platinum and iridium which may accompany it will remain insoluble. The fused mass is treated with 15 c.c. of strong hydrochloric acid, and then with water, and heated on the water-bath. The insoluble residue is separated, washed, ignited in hydrogen, cooled in carbon dioxide, weighed, and added to the main precipitate containing the platinum and iridium, prior to the separation of the latter by means of *aqua regia*. The solution containing the rhodium is reduced with zinc, the deposit washed by trituration with dilute hydrochloric acid, ignited in hydrogen, cooled in carbon dioxide, and weighed as pure rhodium. *Estimation of Iron*—This is effected in the filtrate from the first reduction with zinc by a double precipitation as acetate.

C. A. M.

**Cyanometric Method of Estimating Silver and Halogens in Ammoniacal Solution.** J. Eggert and L. Zipfel. (*Ber.*, 1919, 52, 1177-1185; *through J. Soc. Chem. Ind.*, 1919, 38, 605 A.)—The procedure depends on the fact that silver iodide is only precipitated from very dilute ammoniacal solutions of silver salts by addition of potassium iodide when electrolytes are present in large amount or when the solution is warmed, continuously shaken, or preserved for a long time; otherwise an opalescence of colloidal silver iodide is formed: if potassium cyanide solution is added, the turbidity increases at first and suddenly disappears when the amount of  $CN'$  necessary for the formation of  $Ag(CN)'_2$  has been added. Silver is estimated in ammoniacal solution in the following manner. A known volume of approximately  $\frac{N}{10}$  potassium cyanide solution is diluted with about four times its volume of water and

sufficient ammonia is added to make the solution at least  $\frac{N}{4}$ ; after introduction of a quantity of potassium iodide approximately equivalent to that of the cyanide taken, the silver solution is added to incipient turbidity. Halogens are estimated indirectly by using an excess of silver nitrate solution and titration of the residual silver after filtration of the silver halide. The method can also be applied to the estimation of acids, the silver salts of which are distinguished by sufficient difference in their solubility in ammonia; thus chloride and iodide may be simultaneously estimated in that their sum is determined by the indirect process and the iodide alone estimated in a solution which is sufficiently ammoniacal to retain the silver chloride in the dissolved state. To obtain accurate results, it is necessary that the amount of potassium iodide used as indicator should be approximately equivalent to the amounts of substance taken for titration. The use of potassium iodide in Liebig's method of titration is shown to bring no advantage and, in certain cases, even to lead to false results.

**Estimation of Antimony, Lead, Tin, and Copper, in Alloys.** G. Oesterheld and P. Honegger. (*Helv. Chim. Acta*, 1919, 2, 398-416).—The method depends upon the fact that, on treating the alloy with boiling sulphuric acid, the antimony is dissolved in the trivalent condition, the whole of the tin is dissolved as stannic sulphate, whilst the copper and lead are converted into sulphates, which are partially soluble in the strong acid. On dilution with water the lead separates quantitatively as crystalline lead sulphate, which can be separated and weighed as such. The antimony in the filtrate (or the original solution) may be estimated by titration with potassium bromate, and, after the titration, the liquid is reduced, and the tin and the copper estimated by volumetric methods: One grm. of the alloy is boiled with 20 c.c. of strong sulphuric acid until the sulphur dioxide formed has been expelled, when the liquid is cooled and diluted to about 100 c.c. It is then treated with 5 c.c. of strong hydrochloric acid and the antimony slowly titrated with  $\frac{N}{10}$  potassium bromate solution, using methyl orange as indicator. The titrated solution is allowed to stand for an hour and the deposit of lead sulphate collected in a tared Gooch crucible, which is then heated for fifteen minutes in an electric muffle oven at 500° to 600° C. (not more) to expel all traces of sulphur, cooled and weighed. In the presence of a large proportion of tin an aliquot portion of the filtrate is taken for the estimation of that metal, but when the amount does not exceed 30 per cent. the whole filtrate may be used. It is reduced by adding 80 c.c. of strong hydrochloric acid, and three successive portions of about 3 grm. of zinc turnings, boiled to redissolve the tin, rapidly cooled in water, and immediately titrated with  $\frac{N}{10}$  bromate solution, after the addition of 5 c.c. of potassium iodide solution and 5 c.c. of freshly prepared starch solution. For the estimation of the copper, 1 grm. of the original alloy is treated with 20 c.c. of sulphuric acid, as described, the solution made up to 100 c.c., and cooled, 30 c.c. of about  $\frac{N}{2}$  potassium iodide solution added, and the separated iodine electrometrically titrated with  $\frac{N}{10}$  thiosulphate solution. C. A. M.

**Analysis of Tin Ores.** A. Craig. (*J. Ind. and Eng. Chem.*, 1919, 11, 750-753.)—When an alloy of tin is treated with nitric acid the precipitation is never

complete and the precipitate is always impure: antimony, arsenic, phosphorus, copper, iron, and magnesium may be present in it. If sulphur is present in the alloy the treatment with strong nitric acid will cause the formation of lead sulphate, but this may be avoided by the use of dilute acid (sp. gr., 1.2), digesting on the water-bath and crushing the lumps, if necessary, to assist the decomposition and separation. In filtering the tin precipitate, the filter and funnel should be arranged to preserve the column of liquid in the stem of the funnel, and a little filter paper pulp should be poured on the filter; this will make the stream slower at first, but it prevents clogging by the slimy precipitate. The filtrate is mixed with sulphuric acid and evaporated until fumes of sulphur trioxide come off; water is added equal to 5 c.c. for each 1 c.c. of sulphuric acid, the copper sulphate is dissolved, and the lead sulphate allowed to settle out. Meanwhile, the tin precipitate should be ignited without loss of time, first over a Bunsen flame and then in a muffle with a blast flame until constant in weight. The residue is then fused with about 20 parts of a mixture consisting of 14 parts of potassium carbonate, 10 of sodium carbonate, and 10 of sulphur. The melt is extracted with water, and the precipitate filtered and washed with ammonium hydrogen sulphide. It is ignited, weighed, covered with a little hydrochloric acid, and warmed until the copper and iron are dissolved. The liquid is diluted and filtered on a very small paper, the residue is ignited and weighed. The first residue contains some stannic oxide and silica, and, possibly, fragments of the crucible which remain in the second residue. The difference between these is the correction for oxides insoluble in the fusion. The hydrochloric acid filtrate from the first residue is treated with sulphuric acid, evaporated to fuming, and then diluted; the solution is then combined with that from the tin precipitate. The alkaline filtrate from the sulphur fusion contains all the antimony if it is less than 20 per cent. of the tin, also some of the arsenic. The solution is treated with a slight excess of sodium chlorate and then with half its volume of hydrochloric acid, and boiled down to a small bulk. It is made just alkaline with ammonia, oxalic acid and ammonium oxalate are added and hydrogen sulphide is passed in. The precipitate of antimony and arsenic is dissolved in a minimum amount of 5 per cent. potassium hydroxide solution containing some hydrogen sulphide, the solution is oxidised with sodium chlorate and hydrochloric acid, the excess of chlorine is boiled off, and the liquid titrated with thiosulphate. After titration it is acidified with hydrochloric acid, and the arsenic is precipitated with hydrogen sulphide. Phosphorus may be estimated by adding ammonia to the oxalate filtrate from the antimony and then magnesia mixture, but it is best determined in a separate portion. The ignited tin precipitate is now corrected by deducting from it the oxides insoluble in the fusion, the phosphorus, as  $P_2O_5$ , the antimony, as  $Sb_2O_4$ , and the arsenic, as  $As_2O_5$ . In some cases it is necessary to add to it a small quantity of tin recovered from the electrolyte solution. J. F. B.

#### APPARATUS, ETC.

**Single Deflection Method of Weighing.** P. H. M. P. Brinton. (*J. Amer. Chem. Soc.*, 1919, 41, 1151-1155.)—The method, which cannot be used with balances in which the beam and pan arrests are all released by one operation, is carried out

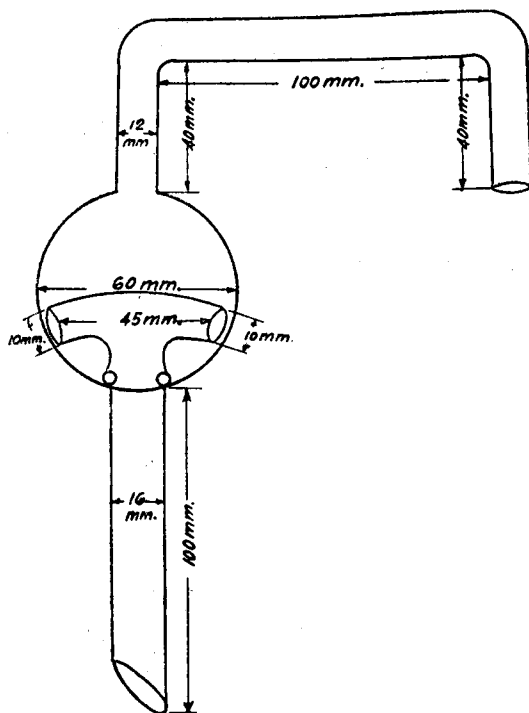


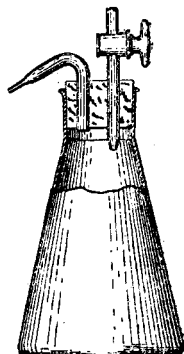
as follows: The balance is given a permanent overload on the left arm by screwing the adjusting nut at one end of the beam, so that, when the beam and pans are released the pointer will swing out from three to seven scale divisions to the right. The pan arrests must be so adjusted that there is no lateral vibration of the pans when released. Before determining the zero point, the stability of the pans is assured by moving the pan-arrest button in and out a few times. The beam is then freed and the pans are next released by a gentle, steady motion. The pointer will swing to the right and the turning point of this single excursion is taken as the zero point. To obtain the weight of any object it is only necessary to add weights until the pointer is caused to swing out to the same point on the scale. The method has been known to the author for ten years and was not new then. It has only once been described in print (Turner, *Chemist-Analyst*, January, 1916) and its originator is unknown. So unorthodox did the system appear that the author refused to try it until recently, but he now shows that the error of observation is negligibly small. The method has been tried in his laboratory by experienced manipulators and by junior students on balances ranging from the best analytical balance to balances with a sensibility of only 2 scale divisions per mgrm.

G. C. J.

**New Form of Distilling Bulb.** J. S. McHargue. (*J. Ind. and Eng. Chem.*, 1919, 11, 670-671.)—The apparatus is shown in the diagram, which is self-explanatory. A drain hole 5 mm. in diameter is blown out on the opposite sides of the stem of the T, 15 mm. from the arms and directly beneath them.

W. P. S.





**Simple Weighing Burette.** D. W. MacArdle. (*J. Ind. and Eng. Chem.*, 1919, 11, 670.)—The apparatus is shown in the sketch; the flask holds about 100 c.c. To use the burette, the flask is tilted, with the tap closed, so that the bent capillary is over the titrating vessel; the solution is forced into the capillary by the heat of the hand and the tap then opened, when the liquid will flow freely.

W. P. S.

#### ERRATA.

- Page 275, line 8, for "pentaminemanganous" read "pentamminemanganous."  
 " 275, " 15, for "hexaminemanganous" read "hexamminemanganous."  
 " 275, " 35, for "pentaminemanganous" read "pentamminemanganous."  
 " 276, " 8, the words "fail to" to be deleted.  
 " 279, " 13 from bottom, for "hexamineferrous" read "hexammineferrous."



#### REVIEW.

**TECHNICAL ANALYSIS OF BRASS AND THE NON-FERROUS ALLOYS.** By W. B. PRICE and R. K. MEADE. 1919. Pp. 376+ix. Second Edition. New York: John Wiley and Sons. London: Chapman Hall and Co., 1919. Price 13s. 6d. net.

The scope of this book is much larger than that indicated by its main title, as it includes, in the introduction, chapters on Engineering Alloys and on Apparatus for Electrolytic Analysis. The larger part of the book is devoted to the methods used in the determination of individual metals and to some applied examples of alloy analysis. Into this second edition has been introduced a chapter on the Control and Analysis of Plating Solutions. The book may be useful at times for reference, but cannot be recommended as a guide to chemists not familiar with the necessary steps in the types of analysis dealt with.

There is evidence of the copying of methods without trial or thought being given to them, as, for example, in the portion dealing with the volumetric determination of tin, where a method suitable for ores is given for the analysis of alloys, without the necessary variations. The reader is instructed to weigh 1 grm. of finely divided alloy fuse with *sodium hydrate* in a thin spun-iron crucible, extract with water and hydrochloric acid, avoiding the use of too much water, as any *gelatinous silica* dissolves best in strong acid.

The hope expressed by the authors that this little book would take a place in non-ferrous chemistry and metallurgy corresponding to that occupied by Blair's "Chemical Analysis of Iron" in the ferrous metals is unlikely to be realised.

C. O. BANNISTER.