

THE ANALYST.

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

A STUDY OF THE DETERMINATION OF POTASSIUM AS THE PERCHLORATE, AND THE SEPARATION FROM SODIUM, ETC.

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(Read at the Meeting, June 2, 1920.)

THE work outlined below is a summary of nearly six years' experience of the perchlorate process, and it is claimed that, given attention to essential details, the results approach to scientific accuracy.

In the course of this work the strength of alcohol is expressed as percentage by volume. "Perchloric acid" means the aqueous acid, and in the experimental work a 20 per cent. solution was used. The formula HClO_4 refers to the absolute acid.

The insolubility of potassium perchlorate in strong alcohol was observed by Sérullas (*Ann. Chim. Phys.*, 1831, **46**, 294), who described an analytical process based on this fact.

Schloessing (*Compt. rend.*, 1871, **73**, 1269) seems to have been the first to publish trial results by the method. He evaporated the solution with perchloric acid nearly to dryness in a sand-bath, treated the cold residue with small quantities of strong alcohol, and decanted. "The more soda present the more sodium perchlorate is retained by the perchlorate of potassium; therefore it is best to dissolve the partly washed perchlorate of potassium in the least possible amount of hot water, and again evaporate to dryness. Two more washings with alcohol complete the washing."

Results given on a mixture of $\text{NaCl} + \text{KCl}$ are remarkably close to the truth. No determination on a pure potassium salt alone was made. The accuracy of these results may be ascribed partly to the use of nearly the minimum amount of alcohol (20 to 40 c.c. in all), and partly to the fact that the presence of sodium perchlorate considerably reduces the slight solubility of the potassium perchlorate in alcohol; in addition, the potassium perchlorate retains slight traces of the sodium salt even after the perchlorate residue remaining after the preliminary washing with alcohol is redissolved and the solution is again evaporated to dryness.

Wense (*Zeitsch. angew. Chem.*, 1891, 4, 691; 1892, 5, 233) used 96 per cent. alcohol containing 0.2 per cent. by weight of HClO_4 as the wash liquid, which considerably reduces the solubility of potassium perchlorate. The perchlorate residue was extracted twice with 10 c.c. of this mixture, and then collected and washed with the same liquid. Then, finally, it was washed with a few c.c. of pure alcohol to free it from traces of adhering perchloric acid. Tared filter papers were used. Drying temperature, 120° to 130° C. "The whole process requires 50 to 75 grms. of alcohol."

Caspari (*Zeitsch. angew. Chem.*, 1893, 6, 68) applied the process to the direct estimation of potash in fertilisers, ashes, etc., containing Fe, Mn, Al, P_2O_5 and alkaline earths. He recommended: (a) Filter tubes with asbestos; (b) wash liquid containing 97 per cent. alcohol and 0.2 per cent. HClO_4 ; (c) two evaporations with perchloric acid, finally to a syrup before treating with wash liquid; (d) extraction of cooled residue with 20 c.c. washing fluid, decanting and repeating extraction with 20 c.c. more; (e) dissolving residue in hot water and re-evaporating, as suggested by Schloessing; (f) transferring with the washing fluid, and finally washing with a few c.c. of pure alcohol. Drying temperature, 130° to 150° C.

These recommendations are improvements, excepting the use of 20 c.c. of wash liquid instead of the 10 c.c. recommended by Wense for each of the two preliminary extractions. The usual descriptions of the perchlorate process follow Caspari as regards the amount of wash liquid for extraction, but ignore nearly all the other details emphasised by him.

D. A. Kreider (*Amer. J. of Science*, 1895, 49, 433; reprinted, *Chem. News*, 1896, 73, 9-17) followed Caspari's details, using pure potassium chloride (0.1 gm.) and also a mixture containing a known amount of potassium chloride. A Gooch crucible is recommended. The results were good. In the case of the pure salt the error was $\frac{1}{10}$ to $\frac{4}{10}$ mgrm. below truth. Total filtrate, close to 50 c.c.

W. A. Davis (*J. Agric. Science*, 1912, 5, 52), made a detailed study of the process. He evaporated the solution once, on a sand-bath, with perchloric acid until it fumed strongly. The perchlorate residue was treated with 95 per cent. alcohol, and after decantation transferred and washed with alcohol to which 0.2 per cent. HClO_4 had been added, and finally washed with about 5 c.c. of pure 95 per cent. alcohol and dried at 100° C. The results are fair, but show somewhat wide variations. At the close of the paper he recommends that, after preliminary extraction with the 20 c.c. alcohol, the rest of the washing should be carried out with a solution of potassium perchlorate in 95 per cent. alcohol, saturated at room temperature.

Thin and Cumming (*J. Chem. Soc.*, 1915, 107, 361) recommend the use of the saturated solution of potassium perchlorate in 95 per cent. alcohol for the washing liquid as suggested by Davis. Beyond stating that the results are accurate they give no analytical data. Their paper is chiefly useful for their solubility determinations of potassium perchlorate in alcohol of various strengths, and in alcohol containing varying amounts of perchloric acid.

Baxter and Kobayashi (*J. Amer. Chem. Soc.*, 1917, 39, 249) have shown that absolute alcohol containing 0.1 per cent. HClO_4 dissolves at 0° C. as little potassium perchlorate as any practicable mixture (1.9 mgrm. per 100 c.c.), although the salt is still appreciably soluble even in this liquid. They recommend washing at a

temperature near 0° C. with a saturated (at 0° C.) solution of potassium perchlorate in the above liquid. They used a platinum sponge crucible and dried at 200° C. in an electric oven. The results were good, but working at 0° C. is obviously inconvenient.

In a later paper (*J. Amer. Chem. Soc.*, 1920, **42**, 735) they agree with the criticism of Gooch and Blake (see next paragraph) that potassium perchlorate may be precipitated from this washing solution when much sodium is present. They modify the process by making a preliminary extraction with 20 c.c. of absolute alcohol, containing 0.1 per cent. HClO_4 , but no perchlorate, and then washing with the perchlorate solution (saturated at 0° C.) already described. Otherwise, the process in detail is the same. A series of good results is quoted. In the presence of much sodium, re-solution of the precipitate in water, and re-evaporation at least once, is necessary.

Gooch and Blake (*Amer. J. Science*, 1917, **44**, 381) have shown that, at ordinary temperatures, the addition of a wash solution saturated with potassium perchlorate, to the perchlorate residue leads to precipitation of some of the dissolved potassium perchlorate, when much sodium perchlorate is present. (*Cf.* Baxter and Kobayashi.) They recommend the use of 97 per cent. alcohol containing 0.1 per cent. HClO_4 as wash liquid throughout the process, and avoid loss, through solubility of the KClO_4 by restricting the amount of wash liquid used. They treat the perchlorate residue first with 10 c.c. only of washing fluid; decant; redissolve the residue and again evaporate when much sodium is present; treat again with 10 c.c., decant, and finally wash with 5 c.c. of the same wash liquid added in portions. In all their determinations the total filtrate was kept at 25 c.c. Repeated evaporation with perchloric acid is desirable if more than 0.2 gm. of $\text{NaCl} + \text{KCl}$ is present. (It will be seen that the final washing with pure alcohol usually prescribed is discarded; this washing with pure alcohol is the chief cause of the low results generally found in the perchlorate method.) The drying temperature is 130° C. If these details are followed, the problem of getting consistently accurate results by the perchlorate process is solved without the use of a saturated perchlorate solution for the washing.

The process I have adopted since 1914 is the same in nearly every detail as Gooch and Blake's.

The perchlorate process has also been applied by some workers to the precipitate of potassium-sodium-cobaltinitrite. This is a useful process when sulphates or tartaric and citric acids are present. Bennett (*ANALYST*, 1916, **41**, 165) used it. The results are good; generally a little higher than truth.

Notes on the Varying Procedures given above.—Wense's suggestion of using 10 c.c. only, of the wash liquid for each washing by decantation has been neglected. I had adopted it before I saw Gooch and Blake's paper. Most text-books follow Caspari's quantities of 20 c.c. each time. This increased amount is probably of little moment in the case for which Caspari describes the method—viz., the direct determination of potash in mixed fertilisers, etc., where considerable amounts of other bases and also phosphoric acid may be present; but when only a pure potassium salt is present, low results will be obtained. The final washing with pure alcohol to remove traces of perchloric acid is unnecessary when asbestos filters are used, and

the precipitate dried at 130° C. or higher. Davis dried at 100° C.; a higher temperature is better.

The wash liquid should contain at least 97 per cent. alcohol after the addition of the perchloric acid, and there is no objection to using absolute alcohol containing perchloric acid. With lower alcohol strengths than 97 per cent. the solubility of the potassium perchlorate increases considerably.

Two evaporations with perchloric acid should be made; if an excess of perchloric is present at the end of the first evaporation, the second evaporation will suffice in all cases. The Gooch crucible is the best filter. At least one solution of the precipitate followed by re-evaporation is necessary, after preliminary extraction with wash liquid, when sodium or other bases are present; otherwise the results may be above the truth. Finally, it is advisable to keep the total amount of wash liquid as low as possible, as too free use of it will make the results low.

Influence of other Substances present: Ammonium Salts must be absent.—The results obtained by Schloessing show that the presence of alkaline earths and magnesia exerts but little effect on the results, and Caspari has shown that it is not necessary to remove phosphoric acid, and that it is only necessary to remove sulphuric acid. This last is absolutely essential, owing to the insolubility of sodium sulphate in alcohol. In his paper Davis shows that fair results are obtained on pure potassium sulphate without removing the sulphuric acid, and states that it is not always necessary to remove sulphuric acid; but he seems completely to have overlooked the point that the removal of sulphuric acid is necessitated in general analysis by the insolubility of sodium sulphate in alcohol, and he himself found that, when magnesium was present as sulphate, the removal of the sulphuric acid was necessary. In a later paper (*J. Chem. Soc.*, 1915, 107, 1680) he recommended the removal of sulphuric acid in all cases except in the analysis of pure potassium sulphate. It is evident that Davis assumed that sodium sulphate on evaporation with perchloric acid behaves similarly to potassium sulphate. This is not the case; the perchloric acid treatment leaves sodium sulphate unchanged. This is a very important point to note, and is referred to below, under "Experimental."

As regards magnesium, Kreider treated 0.15 gm. magnesium carbonate with excess of perchloric acid, evaporated the solution, and treated the cold residue with alcohol, when a perfectly clear solution was obtained.

Practically all perchlorates seem to be freely soluble in strong alcohol except those of potassium, rubidium, caesium, and ammonium. Ammonium perchlorate is slightly soluble in alcohol—about 2 per cent. In using the perchloric process, it is essential to use sufficient perchloric acid to convert completely all the bases present into perchlorates, owing to the insolubility of most chlorides, etc., in alcohol. Kreider found that, to secure a nearly complete separation of phosphoric acid from the potassium, a considerable excess of the perchloric acid should be left upon the potassium perchlorate before it is treated with alcohol.

Textbook Descriptions of the Process.—These, in general, are faulty. Mellor's "Treatise" follows Caspari generally, but omits the re-dissolving and re-evaporation of the residue after the first treatment with the alcoholic fluid. The final washing with pure alcohol is omitted; this is an improvement.

Treadwell (*Quant. Anal. II.*, English edition) describes the process accurately in Caspari's own words, but makes a serious error at the end by saying that, finally, the precipitate is to be washed with 50 to 75 c.c. of pure alcohol. If this is done, the results must be low, unless in the case where a very large amount of sodium is present. This error has arisen through misreading Wense's words, "the whole process requiring 50 to 75 grms. of alcohol," this implying a total filtrate of 60 to 80 c.c. There seems little doubt that this description may have led to the condemnation of the process by some workers who have tried it on a pure potassium salt, following Treadwell's directions, and found the results too low.

The Stassfurt modification of the perchlorate process for crude potassium salts is described by Lunge and Keane (*Tech. Methods of Chem. Anal.*, Vol. I., Part II., p. 530). The details resemble those of Caspari, but the re-dissolving of the perchlorate is neglected. The washing solution is 96 per cent. alcohol, to which 2 per cent. (of 20 per cent.) perchloric acid has been added. Finally, the perchloric acid is removed by washing with a minimum of pure 96 per cent. alcohol. A water-bath is specified for the evaporation; this is unsatisfactory, a higher temperature (120° to 130° C.) is necessary for the final stage of the evaporation, since the perchloric acid does not reach the fuming-point at the temperature of the water-bath. The washing solution, it will be noted, contains only 94 per cent. alcohol and 0.4 per cent. HClO_4 ; 0.2 per cent. HClO_4 is sufficient; the extra amount of acid reduces the alcohol content by an extra 1 per cent.

Perchloric Acid.—Pure perchloric acid, "reagent," has only been obtainable commercially in the last fifteen years. Kreider described a very convenient method of preparing the acid from pure sodium perchlorate by treating it with fuming hydrochloric acid (sp. gr. 1.2), filtering off the sodium chloride precipitated, on asbestos, and concentrating the filtrate to the fuming-point. Such an acid contains about 40 to 50 mgrms. of sodium perchlorate in 1 c.c., and is of 60 per cent. by weight (equal to nearly 1 gm. HClO_4 per c.c.).

Thin and Cumming found that Merck's "pure" perchloric acid (20 per cent.) gave 0.1476 gm. solid residue from 10 c.c. and contained some potassium perchlorate. Another lot of acid gave 0.049 gm. from 10 c.c.

Perchloric acid of reagent purity has been obtainable both from a German, and at least one English source since 1910, such acid leaving only traces of visible matter on evaporation of 10 c.c. and giving no result for a blank when put through the analytical process for potash.

STRENGTHS AND SPECIFIC GRAVITIES OF PERCHLORIC ACID SOLUTIONS.

Specific Gravity.	HClO_4 (Per Cent. by Weight).	Boiling-Point.	HClO_4 grms. per 100 c.c.
1.782 at 15.5° (Roscoe)	100	110° (Roscoe)	—
*1.82 (Roscoe)	71.6	203° (Roscoe)	120
1.12	20	—	22

* Aqueous acid of constant boiling-point, approximating to the composition of the dihydrate $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.

I have found the commercial "pure" 20 per cent. acid free from potash, but a blank analysis gives 1 to 2 mgrms. of residue (per 10 c.c. of the acid) insoluble in alcohol, but this is nearly always found to be silica only. Davis apparently used such an impure acid and did not correct for it in his results.

It is noticeable that, according to Roscoe, the pure acid has a much lower sp. gr. and also a lower boiling-point than the 71 per cent. acid. (*J. Chem. Soc.*, 1863, 16, 82.) From the content of HClO_4 by weight in volume, it is evident that the 70 per cent. acid is nearly five and a half times stronger in HClO_4 than the 20 per cent. acid, when equal volumes are taken. Later workers have used the 20 per cent. acid, while the acid of Kreider, and also of Caspari, was of about 60 per cent. Wash-alcohol, containing 0.2 per cent. HClO_4 , is 1 per cent. weaker in alcohol (when the 20 per cent. acid is used) than the pure alcohol used for the preparation. Kreider has also described the preparation of the purified acid (70 per cent.) by distillation, under reduced pressure. Gooch and Blake in their work used acid prepared in this way of 70 per cent.

Experimental.—In 1914 I had occasion to determine the potash in a mineral water of the Apollinaris type, and used the perchlorate process for this, following the procedure described below. Some further preliminary work showed that the process was accurate, and that it was unnecessary to wash with a solution of perchlorate of potassium in alcohol. The process was also used, in general practice, to check the amount of potash salt in solutions prepared on a manufacturing scale.

Fresenius (*Quant. Anal.*) recommended the use of the filtrate to transfer potassium platinichloride and also magnesium ammonium arsenate to the filter, in order to avoid over-washing. I adopted this procedure for the transference of the perchlorate, to avoid using more than 30 to 40 c.c. of washing fluid in all. The trial analyses were undertaken to find accurately the experimental error of the method, using varied amounts of potassium salt. The publication of Gooch and Blake's paper (*loc. cit.*) confirmed my own results, but the trial-analyses were continued to supplement their work. A few analyses using increased quantities of wash liquid were also made in order to compare the results. A total of 25 c.c. of wash liquid is not always quite sufficient to wash the precipitate thoroughly when considerable amounts of sodium or other salts are present.

Reagents.—The perchloric acid used was a 20 per cent. solution (analytical reagent). Ten c.c. of the acid left, on evaporation and drying at 140°C ., usually about 3 mgrms. of residue. This residue, however, when treated with the alcoholic wash liquid, usually left nothing weighable on the filter. More recently I have found a residue, after filtering, amounting to 0.4 mgrm. per 10 c.c. acid. The trace of insoluble residue is apparently silica. In using this batch of acid, the corresponding correction has been made on the perchlorate obtained in the analysis. The potassium chloride used was Kahlbaum's "K" brand, "for analysis."

Wash Liquid.—Made as follows :

Alcohol, 98 per cent.	100 c.c.
Perchloric acid	1 c.c.

This wash liquid will have a content of 97 per cent. alcohol, and will contain, practically, 0.2 per cent. HClO_4 .

The 98 per cent. alcohol can be easily made by mixing 110 c.c. of absolute alcohol (of not less than 99.5 per cent.) with 100 c.c. of 96 per cent. alcohol.

Process.—In nearly all cases the solution of the salt was evaporated with perchloric acid, three times in all, and in the final evaporation taken practically to dryness. The residue (in the analyses following after No. 3 and No. 3A of Tables I. and II.) was treated with 10 c.c. of wash liquid, stirred well with a flat-headed glass rod, allowed to stand ten to fifteen minutes when sodium was present, occasionally stirring; the solution allowed to settle, and the liquid decanted through a weighed Gooch crucible containing asbestos. When only potassium was present, the precipitate was then rinsed out directly with the wash liquid, in measured quantity, by means of a wash-bottle. When sodium was present the basin containing the residue from the first decantation was placed on the top of the air-oven for a few minutes, till the alcohol was evaporated; then the residue was dissolved in the minimum amount of boiling water, and again evaporated to dryness. The treatment with 10 c.c. of wash liquid and decantation was repeated, and the residue then transferred completely by using the latter 10 c.c. of the filtrate. Finally, a measured volume of wash liquid was added (by the use of a small pipette) in portions, to complete the washing on the filter. The Gooch crucible and contents were then dried for about an hour at 130° to 150° C., cooled for one hour in a desiccator and weighed. After weighing, 2 to 3 c.c. more wash liquid were passed through the filter, and the drying and weighing repeated. The weight was taken as constant when, on washing with 2 to 3 c.c. of liquid, the difference on successive weighings did not vary by more than one or two tenths of a milligram.

In all cases the weighings were made by the method of vibrations; pipettes and weights were calibrated, and the solutions used were adjusted at 15° C., and measured off after being always brought to the same temperature. The usual variations obtained in weighing crucibles, etc., which may easily amount to 0.0003 gm. or more, due to absorption of air and moisture by the glaze of the crucible during weighing, were thus minimised by weighing quickly. On the average, the weighings may be taken as correct within ± 0.0001 gm.

Apparatus, etc.—In nearly all cases porcelain Gooch crucibles of 10 c.c. capacity were used; in one or two instances only, a 20 c.c. quartz "Gooch" was employed. For amounts of potassium perchlorate from 0.4 gm. upwards the 10 c.c. "Gooch" is rather small. The same asbestos felt was used over and over again, the crucible, after finishing an analysis, being washed out repeatedly with boiling acidulated water. After six or eight estimations, the interior of the crucible will be found to be slightly stained yellowish brown, and the weight of the empty crucible will show an increase of 0.1 to 0.2 mgrm., even though the acid gives no weighable residue in the blank process. This colour is apparently due to the action of perchloric acid on the alcohol or on the impurities (*i.e.*, the traces of aldehydes or esters) contained in the alcohol. In practice it is well to ignite the empty crucible containing the asbestos after six determinations have been carried out; then to pass some distilled water through the crucible, and dry at 130° to 150° C. as usual.

It is essential to have proper facilities for drawing off the filtrate conveniently. The usual pressure-flask is quite inconvenient. Filtering direct into a beaker or

flask inside an exhausted bell-jar is satisfactory, but the handiest apparatus is the Gooch filter-tube, No. 1180 in Townson and Mercer's list. This is a wide-mouthed cylindrical separating funnel, with stop-cock at bottom, and a side tube to connect with the pump.

The Wash-Bottle.—It is best to use a wide test-tube for this, as the small amount of wash liquid used makes even a small flask unsuitable. The outlet tube and jet should be made from one piece of glass tubing, as contact with rubber connections is best avoided. The tip of the jet should be drawn out very finely. The portions of wash liquid used should be approximately measured.

It is best to use the wash-bottle in transferring the filtrate, rinsing out directly into the "Gooch"; after nearly all the precipitate appears to be transferred, it is essential to rub round carefully the sides of the dish, by using the tip of a feather as a brush. It is very difficult to know when the dish has been properly cleaned, the alcohol seems to reduce the visibility of the precipitate and the usual rubber-tipped rod is unsuitable for this transference, as the rubber soon gets slightly sticky, owing to the action of the trace of perchloric acid in the washing fluid.

Platinum or quartz dishes are preferable to glass. A white porcelain basin is useless. A blue glazed porcelain basin (Royal Worcester ware) was used in some cases; this is satisfactory for enabling one to judge when all the precipitate has been transferred. But Gooch and Blake have noticed that perchloric acid has a decided action on glass, and the results in the Tables I. and II. seem to show a similar action in the case of the blue glazed porcelain. In such cases the perchlorate of potassium may contain silica.

Evaporation.—A water-bath is unsuitable, since the perchloric acid cannot be concentrated to the fuming-point below 120° C. Davis recommended a sand-bath, which is inconvenient in quantitative work. It is best to use some form of hot air-bath. The simplest device is to use a shallow sand-bath tray, covered with a set of rings, on which the dish is set. The heat is applied by means of a burner with a rose top. With a little practice the temperature is easily adjusted to allow of speedy evaporation, without the liquor ever boiling, even towards the end. In all these test analyses, the air-bath and the dish were placed under an inverted Victor Meyer funnel, so as to exclude dust from the atmosphere.

The following hints on preparing the asbestos felt in the "Gooch" may be useful: Shake up a fair quantity of the prepared asbestos emulsion in water, let the whole settle partially by leaving it to stand two or three minutes. Decant off the liquid containing the finer particles of asbestos into another bottle. Prepare the "Gooch" by running through some of the coarser emulsion, till the perforations are evenly covered. Then add a few c.c. of the finer emulsion to fill up the larger interstices that may be left in the first layer of the felt. Then put in a perforated plate, and add a little more asbestos as before. Such a felt will retain the perchlorate in all cases, even though the previous stirring may have reduced the precipitate to fine powder. With similar precautions, an asbestos felt can be prepared to retain calcium oxalate, and even barium sulphate, and yet to filter quickly under a medium pressure. With this device, a very thin layer of asbestos suffices.

It is sometimes advised to avoid breaking up the precipitate too much, in case it

becomes too fine to be retained by the filter. The writer's opinion is that it is best to stir up thoroughly and grind to powder by the flat-headed rod. In none of these experiments was a cloudy filtrate ever obtained with potassium perchlorate. In one case the filtrate was slightly opalescent, but this was due to a trace of barium sulphate being present in the perchlorate.

In the case of a direct determination of potash in presence of barium, it is advisable to use a large asbestos card, with a hole in the centre, as the support for the dish instead of the rings. This will partly, at least, deflect the products of combustion of the gas away from the dish, and so help to prevent the formation of any considerable quantity of barium sulphate.

TABLE I.—POTASSIUM ONLY PRESENT.

No.	Potassium Chloride taken (Grm.).	Potassium Perchlorate obtained (Grm.).	Vessel.	Temperature (C.).	Volume of Filtrate (c.c.).	KCl found (Grm.).	Procedure.	Potash Salt recovered (per Cent.).
1	0.2456	0.4551	Glass	13°	60	0.2449	} 20 c.c. + 20 c.c. + washings	
2	0.1368	0.2544	"	13°	60	0.1369		
3	0.1368	0.2539	"	13°	60	0.1366		
4	0.1368	0.2544	Quartz	10°	25	0.1369	} 10 c.c. decanted and precipitate rinsed out by wash-bottle } Filtrate occasionally used to transfer the precipitate	100.07
5*	0.3249	0.6043	"	10°	35	0.3252		100.09
6*	0.3935	0.7305	"	10°	35	0.3931		99.90
7*	0.6673	1.2424	Glass	10°	35	0.6685		100.18
8	0.0988	0.1829	Quartz	21°	27	0.0984		99.60
9	0.0988	0.1834	"	23°	25	0.0987		99.90
10	0.0273	0.0505	"	5°	25	0.0272		} Average 99.96
11	0.0131	0.0242	"	15°	25	0.0130		
12	0.0122	0.0230	"	13°	25	0.0124		
13	0.0122	0.0229	"	13°	25	0.0123		
14	0.0122	0.0227	"	13°	25	0.0122		
15	0.0122	0.0230	Blue glazed porcelain	13°	25	0.0124		
16	0.0152	0.0281	Quartz	21°	25	0.0151		
17	0.0152	0.0282	"	24°	25	0.0152		
18	0.0061	0.0113	"	15°	25	0.0061		
19	0.0062	0.0115	"	15°	27	0.0062		
20	0.00304	0.0055	"	15°	25	0.00296		
21	0.00306	0.0055	"	15°	25	0.00296		

The arrangement of results is in descending order of magnitude, according to the amount of KCl taken, and the results can be directly compared with the corresponding numbers of Table II. The usual order of working was to make two or more analyses of each solution of potassium chloride made up, then, taking the same amount of solution, to add the NaCl as shown in Table II.

* KCl in Nos. 5, 6, 7 weighed off separately.

TABLE II.—POTASSIUM IN PRESENCE OF SODIUM.

No.	KCl taken (Grm.)	NaCl taken (Grm.)	KClO ₄ weighed (Grm.)	Temperature (C.)	Volume of Filtrate (c.c.)	KCl found (Grm.)	Treatment of Perchlorate Residue.*	Potash recovered (per Cent.)
2A	0.1368	0.13	0.2525	13	100	0.1359	} 20 c.c. + 20 c.c. + washings. Not redissolved	
3A	0.1368	0.20	0.2547	13	90	0.1371		
4A	0.1368	0.2	0.2562	5	30	0.1379	10 c.c. + 10 c.c. + washings. Not redissolved Redissolved " " " " " " " " Not redissolved Redissolved " " Not redissolved Redissolved	100.22 100.20 100.14 100.10 99.8 Average 100.09
4A 1	0.1368	0.2	0.2547	5	30	0.1371		
5A †	0.3511	0.3	0.6538	10	35	0.3518		
5A 1 †	0.2083	0.5	0.3877	10	35	0.2086		
8A ‡	0.0988	0.2	0.1838	20	27	0.0989		
9A	0.0988	0.2	0.1833	21	28	0.0986		
10A	0.0273	0.2	0.0512	10	32	0.0276		
10A 1	0.0273	0.2	0.0502	10	30	0.0270		
10A 2 ₁	0.0273	0.2	0.0505	10	32	0.0272		
12A	0.0122	0.5	0.0242	15	30	0.0130		
13A	0.0122	0.3	0.0236	15	33	0.0127		
14A	0.0122	0.3	0.0234	15	30	0.0126		
15A	0.0122	0.2	0.0221	15	30	0.0119		
18A	0.00611	0.12	0.0114	15	30	0.00613		
20A	0.00305	0.13	0.0056	15	27	0.00301		
22§	0.4590	0.5	0.8622	15	35	0.4639	Not redissolved	
23§	0.5096	0.5	0.9618	15	35	0.5175	" "	
24	—	0.5	0.0001	15	35	0.0000	" "	

* 4A to 23 inclusive—10 c.c. + 10 c.c. + washings. Transferred by filtrate from second 10 c.c.

† KCl weighed off separately.

‡ Through not having a "Gooch" crucible prepared, the perchlorate, after treatment with 10 c.c. of wash liquid, stood all night before filtration. Glass dish used for 2A and 3A. Green glazed dish for 5A. Quartz dish for all others. The term "redissolved" means that the residue after the first decantation was dissolved in hot water and again evaporated to dryness.

§ In Nos. 22 and 23 the errors on KCl are respectively: +0.0049 and +0.0079. This shows the necessity of redissolving the residue as described, in the case of much sodium being present. Baxter and Kobayashi found a somewhat similar error.

In Table III. the KClO₄ was redissolved and the solution again evaporated (after the first decantation), $\frac{1}{2}$ to 1 c.c. more perchloric being added. The precipitate was transferred by the second portion of the filtrate.

A. Taken to dryness, treated with 10 c.c. of washing fluid, decanted. After the re-evaporation, 10 c.c. of washing fluid again used and decanted.

B. Taken to a moist pastiness, 10 c.c. of absolute alcohol added and decanted; 10 c.c. again added to the pasty residue on re-evaporation with addition of a little perchloric acid, and the decantation repeated.

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C. Taken to dryness, 0.2 c.c. perchloric acid added, well stirred, then 10 c.c. of 98 per cent. alcohol added, and this treatment repeated. Results good.

D. Same as C, except that 12 c.c. of absolute alcohol used each time in place of 98 per cent. Results too high.

E. Same as C, but using double the amount of perchloric acid, 0.4 c.c. each time.

F. Same as B, using 15 c.c. of 98 per cent. alcohol for each decantation.

TABLE III.—POTASSIUM IN PRESENCE OF SODIUM PHOSPHATE.

No.	KCl taken (Grm.)	Na ₂ HPO ₄ .12H ₂ O (Grm.)	KClO ₄ Weighed (Grm.)	Temperature (C.)	Volume of Filtrate (c.c.)	KCl found (Grm.)	Error on KCl (Grm.)	Process (see above).	Potassium Salt recovered (per Cent.).
1	0.0988	0.4	0.1878	15	35	0.1010	+0.0022	A	
2	0.0988	0.26	0.1834	20	29	0.0987	-0.0001	B	
3	0.0988	0.4	0.1842	20	40	0.0991	+0.0003	B	
4	0.0988	0.4	0.1828	18	30	0.0984	-0.0004	B	
5	0.0988	0.4	0.1838	16	26	0.0989	+0.0001	C	
6	0.0988	0.4	0.1834	16	30	0.0987	-0.0001	C	
7	0.3447	1	0.6613	15	45	0.3558	+0.0111	D	
8	0.3447	1	0.6617	15	45	0.3560	+0.0113	D	
9	0.3447	1	0.6436	13	46	0.3463	+0.0016	E	
10	0.3447	1	0.6397	13	46	0.3442	-0.0005	F	99.86
11	0.3447	1	0.6420	12	45	0.3455	+0.0008	F	100.24
12	0.3447	1	0.6408	10	49	0.3448	+0.0001	F	100.01
									Average 100.03

NOTES TO TABLE III.—In presence of phosphoric acid it is evidently unsafe to evaporate the perchloric solution to complete dryness, as the phosphoric acid, if nearly completely dehydrated, dissolves very slowly in the wash liquid, and cannot be completely washed out of the precipitate in such cases. (See No. 1, Table III.) Kreider recommends in this case that a considerable excess of perchloric acid should be left in contact with the residue before treatment with alcohol. Caspari, in describing his process for the case of fertilisers, etc., where phosphoric acid and alkaline earths are present, evaporated the solution with perchloric acid to "syrupiness" only, and recommends the avoidance of evaporating off too much perchloric acid. This means that varying amounts of water (in the perchloric acid) will be left on the residue, and hence, on treatment with the washing fluid, the alcoholic strength of the latter will be considerably reduced by an indefinite amount, varying with the excess of perchloric acid left on the residue.

For this reason the expedient was tried of taking the residue first to dryness, and then moistening it with 0.1 or 0.2 c.c. of perchloric acid, and adding 10 c.c. of pure strong alcohol of 98 per cent., so as to keep the alcoholic strength of the liquid in contact with the precipitate as near 97 per cent. as possible. (Procedure C.) Final washings were made with the usual mixture.

This procedure gives good results (Nos. 5 and 6, Table III.), but when tried on

larger quantities of sodium phosphate the results were considerably too high (see Nos. 7 and 8, Table III.). Process F, however, gives good results. It seems best, then, to evaporate to a moist pasty condition when much phosphoric acid is present, and to treat the residue with 15 to 20 c.c. of 98 to 100 per cent. alcohol for each decantation. Finally to wash with the usual wash liquid. The free phosphoric acid present seems to have no effect on the solubility of the potassium perchlorate in the washing fluid.

Determination in Presence of Magnesium :

1. Taken 0.0988 gm.	KCl + 0.07 gm. MgO	Found 0.1050 gm.	KCl.
2. ,, 0.0988 ,,	KCl + 0.2 ,, MgO	,, 0.0990 ,,	KCl.
3. ,, 0.0988 ,,	KCl + 0.2 ,, MgO	,, 0.0990 ,,	KCl.

Filtrate in each case—32 c.c. First residue in each case redissolved after first decantation with wash liquid.

The result of No. 1 is too high. On washing with 5 to 10 c.c. more wash liquid the loss was but slight, and the perchlorate still showed the presence of magnesium. This is probably due to some over-heating in trying to carry the evaporation to dryness. When fumes of perchloric acid had nearly ceased coming off, the residue was still pasty while hot, and the temperature was carefully raised to get nearly complete dehydration. It is probable that magnesium perchlorate, which seems to crystallise with a considerable amount of water of crystallisation, partially decomposes before complete dehydration can be effected, some magnesium oxide being formed. Magnesium chloride behaves in this manner, and, apparently, the perchlorate of magnesium resembles the chloride in this respect. On account of this behaviour, in Nos. 2 and 3 above, the evaporation was stopped when the fumes of perchloric acid were still just faintly visible. The pasty residue so obtained sets solid when removed from the heat, and, when cold, forms a hard cement-like mass. It is best to add the 10 c.c. of wash liquid to this, and to set aside for an hour or two before attempting to break up the mass. Any premature attempt at stirring up the mass will inevitably lead to loss by splashing. It is evident from the note on Experiment 1 above, that the washing must be complete, since passing more wash-liquid through the Gooch, after drying at 130° to 150° C., will have but little effect in removing any magnesium left on the perchlorate, as the magnesium will, after the drying, be partly present as magnesium oxide.

Separation from Calcium.—Calcium, evidently, does not interfere with the process. In the evaporation the mass of perchlorates obtained (which is semi-fluid while hot, although fumes of perchloric acid have almost ceased) sets to a hard mass, and the disintegration of this by the wash liquid is best carried out as described under magnesium.

Taken 0.0988 gm.	KCl + 0.07 gm. CaCO ₃	...	Found 0.0986 gm.	KCl	} Filtrate 30 c.c.
,, 0.0988 ,,	KCl + 0.14 ,, CaCO ₃	...	,, 0.0990 ,,	KCl	

In Presence of Calcium and Magnesium together.—Taken 0.0988 gm. KCl + 0.07 gm. CaCO₃ + 0.07 gm. MgO. Found 0.0985 gm. KCl. Filtrate, 30 c.c.

In Presence of Barium.—Barium *per se* does not affect the results, but the con-

version into perchlorate must be complete, since barium chloride is very insoluble in alcohol; still, in practice, for accurate results, it may be advisable to remove the barium when considerable quantities are present, unless the evaporation can be carried out on some form of electrically heated radiator; otherwise, the potassium perchlorate may contain appreciable amounts of barium sulphate, owing to the gas. At a very early stage of these test analyses, the influence of barium was investigated, but the experiment failed, owing to this cause. After the first evaporation, on adding water to redissolve, the residue gave a cloudy solution, which was due to the formation of barium sulphate.

In the results below, the evaporation was carried out on the air-bath described, using a large asbestos card to deflect the products of the burnt gas away from the liquid. Even then, traces of barium sulphate were present in the perchlorate weighed.

1. Taken 0.0122 gm. $\text{KCl} + 0.2 \text{ BaCl}_2 \cdot 2\text{H}_2\text{O}$. Found at first 0.0126 gm. KCl . Corrected by deducting BaSO_4 present, 0.0123 gm. KCl .

2. Taken 0.0062 gm. $\text{KCl} + 0.1 \text{ BaCl}_2$ cryst. $+ 0.2 \text{ MgCl}_2$ cryst. $+ 0.05 \text{ CaCl}_2$ cryst. Found 0.0057 gm. KCl . In this last case the filtrate was slightly opalescent, probably a trace of BaSO_4 was present, which passed through the asbestos.

Determination of pure Potassium Sulphate.—Davis found that the direct estimation of pure potassium sulphate was possible, and the following analyses were therefore tried.

It is obvious that, on evaporating potassium sulphate solution with the perchloric acid, free sulphuric acid is liberated, and that the free sulphuric acid cannot be removed by evaporation without reversing the reaction. For this reason the evaporation was carried out at as low a temperature as would suffice to drive off the perchloric acid in fumes. This leaves the residue of perchlorate quite moist, since the free sulphuric acid at this temperature must still be in a fairly dilute condition. On now adding the wash liquid to this moist residue, a considerable reduction of the alcoholic strength will take place, and somewhat low results may be expected. In analysis 1 below, the ordinary wash liquid (10 c.c.) was used to pour on the residue and decanted, whilst in analysis 2 absolute alcohol (10 c.c. containing 0.2 per cent. HClO_4) was used, to compensate somewhat for the reduction in the strength of the alcohol, the remaining washings, etc., being carried out with the usual wash liquid:

1. Taken 0.1072 gm. K_2SO_4 . Found 0.1066 gm. Filtrate 25 c.c.

2. Taken 0.6704 gm. K_2SO_4 . Found 0.6664 gm. Filtrate 30 c.c.

It will be noted that these results are somewhat low for the reason given above. Davis, using 0.100 gm. K_2SO_4 , recovered 99.1 per cent. in two cases.

Davis's results on a solution containing 0.04 gm. $\text{KCl} + 0.01$ gm. K_2SO_4 were fairly satisfactory, but in stating that it is not always necessary to remove sulphate, he completely overlooked the fact that this removal is necessitated by the insolubility of sodium sulphate in alcohol, and that sodium sulphate is not decomposed into sodium perchlorate by evaporating with perchloric acid. The reason for this difference in behaviour is easily found in Berthollet's law. Potassium perchlorate, being the more insoluble salt, is precipitated, while the opposite is the case with the sodium salt, sodium perchlorate being more soluble than the sulphate.

It is fairly evident, then, that if we take a mixture of potassium sulphate and sodium chloride, high results may be expected, owing to the sodium sulphate being formed. To prove actually by experiments that such is the case, the following analyses were carried out :

1. Taken 0.2627 gm. K_2SO_4 + 0.06 gm. NaCl. Found 0.3099 gm. K_2SO_4 . Error + 0.0472 gm.

2. Taken 0.2592 gm. K_2SO_4 + 0.05 gm. NaCl. Found 0.2975 gm. K_2SO_4 . Error + 0.0383 gm.

On calculating the NaCl taken into its equivalent of sodium sulphate, it was found that this figure came within a few milligrams of the difference between the potassium perchlorate actually weighed and the theoretical amount of perchlorate. It seems conclusive that the error shown in the results is due to the presence of normal sodium sulphate. It is important to notice that evaporation of a solution of sodium sulphate with perchloric acid leaves the sulphate of sodium quite unchanged.

In Presence of Ferric Salts.—Taken 0.3447 gm. KCl + 0.1 $FeCl_3$. Found 0.3445 gm. KCl. Filtrate 32 c.c.

The solution was evaporated with perchloric acid twice, and in the second evaporation was taken nearly to complete dryness, treated with 10 c.c. of wash liquid, decanted, and the perchlorate transferred as usual, without a previous re-crystallisation. It was noticed that the yellow colour of the solution gradually became weaker as the solution approached dryness, and that in the second evaporation the solution was colourless throughout. The residue obtained was pure white, but on treating with the wash liquid the strong yellow colour of the solution reappeared. After washing and drying the perchlorate was perfectly free from any yellow tint. It seems obvious, then, that no possible contamination of the perchlorate with ferric oxide need be feared.

Aluminium perchlorate, also, is perfectly soluble. It is possible, however, that any overheating of the dry residue might lead to high results in the case of iron and aluminium. But if the solution is evaporated as described above, there would seem to be no possibility of this occurring.

In Presence of Citric and Tartaric Acid.—Caspari stated that the process is suitable in such cases, and therefore some trials were made on a specially purified potassium hydrogen tartrate (free from traces of calcium and sulphates).

On carrying out the process as usual, it was found that, in trying to evaporate off the perchloric acid, the mass swelled and turned brownish-black. In another trial the solution was evaporated as far as possible on the water-bath, then transferred to the air-oven at a temperature of about 110° C. Even at that temperature the charring commenced. The following result was obtained by using a very slight excess of perchloric acid over the theoretical amount (0.5 c.c.) and the solution was evaporated, as far as possible, on the water-bath only. The residue was still semi-fluid; 10 c.c. of pure 98 per cent. alcohol were added, and decanted. The transference and washing were then carried out with the usual washing fluid. The results are low, as must be expected, since the perchloric acid cannot be concentrated very far on the water-bath.

In this case it would seem preferable to apply the cobaltinitrite process for the

precipitation of the potash, treating the precipitate then obtained with perchloric acid as usual, but no trial of this process was made.

Taken 0.1005 gm. $\text{KHC}_4\text{H}_4\text{O}_6$. Found 0.0994 gm. Filtrate 30 c.c.

Citric acid behaves similarly to tartaric acid in the evaporation.

Analysis of Samples supplied by Mr. Bertram Blount.—Early in 1919 a selection from the results of Tables I. and II. was sent to Mr. Blount, with the request that he would send a few samples on which to check the degree of accuracy obtainable by the procedure given. Mr. Blount kindly sent some samples. Nos. 1 and 2 were stated to be mixed chlorides of potassium and sodium.

Sample 1 was analysed as received; transferred from the sample tube to a weighing-bottle and the amounts taken weighed off by difference.

The following results were obtained:

	Samples Weighed off separately.	Equal Volumes of the same Solution used.
No. 1. KCl per cent.	36.42, 36.13, 36.66.	36.14, 36.32, 36.11.
Average of six results	...	36.30 per cent.
By platinum process (Mr. Blount)	...	36.40 per cent.

As the above six individual results showed rather a wide divergence between the minimum and maximum found, the whole of sample 2 was rapidly mixed in a mortar before transferring to a weighing-bottle, and all the weighings-off were done immediately.

The results on Sample 2 were:

	Samples Weighed off separately.	Equal Volumes of same Solution used.
No. 2. KCl per cent.	75.64, 75.38.	75.45, 75.54, 75.62.
Average of five results	...	75.53 per cent. KCl.
By platinum process (Mr. Blount)	...	75.53 per cent. KCl.

Series A, B, C, D. Determination of KCl and NaCl in a solution containing also chlorides of Al, Mg, and Ca.

This was done in order to show what results might be expected in the determination of the alkalis in a complex mixture, after removing all other bases, and isolating the mixed alkaline chlorides; and to compare results with a direct determination of the potash without previous removal of the other bases. Great care was taken to eliminate the Ca, Mg, etc., as completely as possible before weighing mixed chlorides, and, after the weighing, the chlorides were dissolved in a little water and any residue ignited, weighed, and its weight deducted from the weight of mixed chlorides. Silica beakers were used for the precipitations involved, and the solution of the alkaline chlorides was evaporated in a large quartz dish. Results were corrected for the sodium chloride found in blank determination on the water and reagents, of which measured amounts were used in the analyses.

19.95 c.c. of solution taken = 0.1805 gm. KCl, 0.1917 gm. NaCl (= 0.3722 gm. NaCl + KCl), 0.005 gm. Al, 0.04 gm. CaCO_3 , 0.04 gm. MgO in hydrochloric solution.

In A, magnesium was removed by barium hydroxide.

In B, magnesium was removed by alcoholic ammonium carbonate (Gooch and Eddy).

In C one gm. of H_2SO_4 added to the solution measured off; precipitated by BaCl_2 at beginning. Magnesium removed by alcoholic ammonium carbonate.

In D, *Direct* determination of potash.

In A, the results approach the theoretical quantity ; in B, a little higher.

In C, the results are low, but this is unavoidable owing to the inevitable adsorption of alkaline chlorides by the barium sulphate. If the precipitation of sulphuric by benzidine could be applied in such cases, it would be an advantage. Here also the cobaltinitrite process and subsequent treatment of precipitate by perchlorate process may be used (*cf.* Bennett *loc. cit.*).

In D, the results show that the direct determination of potash gives good results.

	KCl + NaCl found (Grm.)	KCl found (Grm.).	NaCl by Difference (Grm.).	Mean KCl (Grm.).	Mean NaCl (Grm.).
A	0.3716, 0.3731, 0.3725	0.1803, 0.1807, 0.1812	0.1913, 0.1924, 0.1913	0.1807	0.1917
B	0.3738, 0.3726	0.1823, 0.1819	0.1915, 0.1917	0.1821	0.1911
C	0.3637, 0.3648, 0.3690	0.1740, 0.1761, 0.1773	0.1897, 0.1887, 0.1917	0.1758	0.1900
D	—	0.1814, 0.1815	—	0.1814	—

Note.—The results under C confirm the general conclusion that more potash is adsorbed by barium sulphate than soda.

Solubility of Potassium Perchlorate in the Washing Solution.—The following table gives the results of some careful determinations of the solubility of potassium perchlorate in the washing fluid, made as described, and containing 97 per cent. alcohol and 0.2 per cent. HClO_4 :

Temp. C.	Mgrms. per 100 c.c. of Saturated Solution.	Mgrms. per 100 grm. of Solution.	Solubility by Weight in Volume.	Solubility by Weight in Weight.
10°	2.3	2.9	1 : 47,000	1 : 35,000
14°	3.2	3.9	1 : 32,000	1 : 25,000
15°	3.9	4.8	1 : 26,000	1 : 21,000
17.5°	4.1	5.1	1 : 24,000	1 : 19,000
24°	7.3	9.1	1 : 14,000	1 : 11,000
26.5°	11.1	13.6	1 : 9,000	1 : 7,500

The figures by weight in weight have been calculated, taking the sp. gr. of the washing fluid as 0.807.

Most of these results are the average of two closely agreeing duplicate estimations, and the figures are a very fair approximation to the truth when the small amounts of substance actually present are taken into consideration. All results were obtained by evaporating 100 c.c. of the saturated solution, filtered at room temperature, to dryness, transferring the residue by means of a little hot water to a platinum-shaped quartz crucible, evaporating, adding a drop of sulphuric acid, igniting strongly, and weighing as sulphate. This last procedure is necessary owing to the separation

of carbonaceous particles when the alcohol has been evaporated off, so preventing the direct weighing of the residue on evaporation as potassium perchlorate. The weighing of the potassium sulphate was done with the greatest care to 0.0001 gm.

Loss by Solubility of Potassium Perchlorate.—It is obvious that the actual amount lost in washing, under practical conditions, is of more importance than the true solubility of KClO_4 . The following experiments show that, under such practical conditions of washing, the actual loss to be expected is but slight, except when the room temperature rises to 20° C. From the results of Table I. on pure potassium chloride, it is obvious that the mere stirring up of pure potassium perchlorate with the wash liquid and decantation (twice, with 10 c.c. each time) causes no appreciable loss, so that the loss by continued washing of the precipitate on the asbestos is the chief cause of low results.

TWENTY C.C. QUARTZ "GOOCH" USED.

A. Filtered slowly.

Temp. C.	Potassium Perchlorate in "Gooch" Crucible. (Grm.)	Time of Filtration Per 100 c.c. (Minutes.)	Loss = KClO_4 dissolved out per 100 c.c. (Grm.)
10°*	0.64 approx.	6	0.0014
15°	0.64	6	0.0015
15°	0.64	6	0.0017
19°†	0.64	6	0.0021
19°	0.64	6	0.0020
21°	0.64	6	0.0022

B. Filtered more rapidly.

15°	0.64	3	0.0012
15°	0.64	3	0.0015
15°	0.64	3	0.0009
21°	0.64	3	0.0016

WITH VARYING AMOUNTS OF POTASSIUM PERCHLORATE (10 C.C. "GOOCH"
CRUCIBLE USED.)

15°	0.03	6	0.0005
15°	0.05	6	0.0006
15°	0.09	6	0.0008
15°	0.2	6	0.0012
21°	0.2	6	0.0015

* On passing the filtrate through the crucible again the loss was nil.

† On passing the filtrate through the crucible again the loss was 0.0002 gm.

	KClO ₄ Dissolved Per 100 c.c. (Average.)
Thin and Cumming, using wash liquid containing 97·8 per cent. alcohol and 0·2 per cent. HClO ₄ found	1·3 mgrms.
Thin and Cumming, using wash liquid of pure 98·8 per cent. alcohol found	4·7 „
(The amount of KClO ₄ in the Gooch was 0·37 grm. and temp. 20° to 22° C.)	
Davis, using wash liquid containing 94 per cent. alcohol and 0·2 per cent. HClO ₄ found	2·4 „
Davis, using wash liquid of pure 95 per cent. alcohol found	14·6 „
(Weight of precipitate and temperature not given.)	

Comparison of Platinum with Perchlorate Process as regards Loss in Washing.—Davis found that 100 c.c. of 80 per cent. alcohol dissolved out in washing 4·2 mgrms. K₂PtCl₆, equivalent to a loss of 1·3 mgrm. KCl. Now the highest loss of perchlorate I have found per 100 c.c. of washing fluid used = 2·1 mgrms. (at 21° C.), equivalent to a loss of 1·1 mgrm. KCl. (Working at 15° C. the loss [perchlorate process] would be about 0·7 mgrm. KCl.) Evidently the use of the wash liquid described in this paper makes the perchlorate process quite as accurate as the platinum one, and in both cases washing with excessive amounts of liquid will tend to make the results low.

Loss on Washing KClO₄ with a Mixture in Equal Volumes of above Washing Liquid and Pure Ether.—KClO₄ present, 0·64 grm. Time of filtration, six minutes.

Loss per 100 c.c. at 14° C., 0·0008 grm.; at 15·5° C., 0·0008 grm. These figures show a considerable reduction in the solubility when compared with A above.

In this last mixture I find that sodium perchlorate dissolves freely and rapidly.

My thanks are due to Mr. Blount for his helpful interest in this work, and also for his kind permission to give his results as obtained by the platinum process.

These analyses were carried out in the laboratory of Messrs. R. Fry and Co., Ltd., of Brighton.

ADDITIONAL NOTE ON THE OFFICIAL METHOD FOR FERTILISERS, 1918.

(Leaflet 18 of the Board of Agriculture and Fisheries.)

Since 1918 the perchlorate method has been given as an alternative to the platinum process. I here summarise the details and append criticisms.

A preliminary treatment: preparation of the solution for potash estimation.

1. *Potash Salts containing Sulphates.*—The solution is precipitated by barium chloride, and the excess of this removed by the least possible excess of sulphuric acid. An aliquot part of the filtrate is evaporated with hydrochloric, residue dissolved, filtered, and submitted to either the platinum or perchlorate process.

Criticism.—This is a correct treatment if the platinum process is used, but if perchlorate method is used it is better to allow the slight excess of barium chloride to remain, or else traces of the sulphates of sodium, calcium, and magnesium may be

found with the perchlorate weighed. Attention is again drawn to the presence of traces of barium sulphate in the precipitate in such cases.

2. For flue dust: guanos and mixed fertilisers. The preparation of the solution will eliminate nearly everything but sodium and potassium, and may be regarded as satisfactory.

B. Perchlorate Process.—Two evaporations with perchloric acid are prescribed “till white fumes are copiously evolved,” 20 c.c. of 95 per cent. to 96 per cent. alcohol are now added. After stirring and allowing to settle, the liquid is decanted, draining off as completely as possible; a saturated solution of potassium perchlorate in pure alcohol of same strength is used to transfer and to wash precipitate completely. Drying temperature 100° C.

Criticism.—The repeated evaporation with perchloric acid is a good feature. Final evaporation to dryness, or till fumes of perchloric acid have nearly ceased, would be an improvement. A higher percentage alcohol, 97 per cent. at least, should be used. The method I have described is preferable—viz., evaporation to dryness, treatment with 10 c.c. of 97 per cent. alcohol, containing 0.2 per cent. perchloric acid, decantation, warming to drive off alcohol, redissolving in boiling water and again evaporating, a second treatment with 10 c.c. of the same liquid, decanting off, transferring by use of the filtrate to a Gooch, and finally washing with the same perchloric alcohol in small portions (altogether 10 to 15 c.c. for final washings), and drying at 130° C. If, however, suitable apparatus for drawing off the filtrate is not available, then the process may be followed up to the second decantation, and for the rest of washing a saturated solution of potassium perchlorate in alcohol preferably containing 97 per cent. and 0.2 per cent. perchloric acid is used. The precipitate is filtered off, on a Gooch crucible, and dried at 130° C. If filter papers are used, then a neutral solution of potassium perchlorate in alcohol must be employed (to wash out the traces of perchloric remaining), and the drying temperature should be about 120° C.—i.e., as high as the paper will stand without charring. Ten c.c. of 97 per cent. alcohol dissolve about 2 grms. of sodium perchlorate, and alkaline earth perchlorates are also easily soluble. Therefore much washing is unnecessary.

It is important, if the official process is used, that the 20 c.c. of alcohol added should be drained off very completely before the perchlorate solution in pure alcohol is added. Otherwise the trace of HClO_4 remaining will precipitate 2 to 3 mgrms. of KClO_4 from the washing solution. This possibility is avoided if the perchlorate wash solution is made with alcohol containing perchloric acid.

A moderate excess of perchloric acid is sufficient for official process; 10 c.c. of 20 per cent. perchloric will generally suffice for one gram of substance taken.

It is best to use pure duty-paid alcohol. Industrial methylated spirits (strongest) contain an indefinite amount of water, and are, also, too dilute.

Joseph and Martin (*J. Soc. Chem. Ind.*, 1920, 39, 91,) record a violent explosion on concentrating the filtrate from the perchlorate precipitate to low bulk, in order to estimate sodium directly, in the ash of papyrus. There does not seem to be any danger in the determination of potassium, and Schloessing determined the NaCl in mixtures of pure $\text{KCl} + \text{NaCl}$ by evaporation of the filtrate from the

potash, and finally weighing as the sulphate of sodium, apparently without accident.

NOTE.—While Baxter and Kobayashi have shown that at 0° C. the solubility of potassium perchlorate in alcohol containing 0.1 per cent. HClO_4 is practically the same as in alcohol containing 0.2 per cent., still, their own figures for the solubility at 21° C. show that the 0.2 mixture dissolves *less* than the 0.1 per cent. mixture at room temperatures.



ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Free Acetic Acid in Acetylsalicylic Acid. A. N. Smith. (*Pharm. J.*, 1920, 105, 90-94.)—One grm. of the sample is spread in a thin layer on the surface of a piece of fine muslin tied over the top of a funnel 4 inches in diameter; the stem of the funnel is fitted in a hole in a glass plate, and a bell-jar is placed over the whole. A tube leading from the top of the bell-jar extends to the bottom of a vessel containing a layer of water, and this vessel is connected with a water-pump. Air, free from carbon dioxide, is aspirated slowly through the apparatus for one hour, and the acetic acid absorbed in the water is then titrated. Salicylic acid does not volatilise under these conditions. It is suggested that the maximum permissible limit for free acetic acid in acetylsalicylic acid should be 0.05 per cent., and for free salicylic acid 0.1 per cent., and double these amounts for tablets of the substance.

W. P. S.

Assay of Aconite Preparations. E. J. Chappel and N. L. Allport. (*Pharm. J.*, 1920, 105, 94.)—Fifteen c.c. of the liniment or 100 c.c. of the tincture are evaporated at a low temperature to remove most of the alcohol, 5 c.c. of 10 per cent. sulphuric acid and 20 c.c. of water are then added, the mixture transferred to a separating funnel and extracted with two successive quantities of 20 c.c. of petroleum spirit (b.p. 40° to 60° C.). The united petroleum spirit extracts are washed twice with water; this water is added to the acid solution, which is then rendered ammoniacal and extracted four times with ether. The ethereal extracts are washed once with water, evaporated to dryness, the alkaloidal residue is dried at a low temperature to ensure removal of all ammonia, and then titrated in the usual way.

W. P. S.

Estimation of Allyl Mustard Oil in Black Mustard. D. Raquet. (*J. Pharm. Chim.*, 1920, 22, 92-93.)—By digesting mustard flour with dilute alcohol at 30° to 35° C. for an hour the same result is obtained as after six hours' extraction with cold alcohol, but maceration with water, as prescribed by the French Codex,

gives inaccurate results. By heating the mixture of ammoniacal silver nitrate and mustard oil for an hour on the water-bath the whole of the sulphur will be converted into silver sulphide. These modifications of the Codex method will increase the yield of mustard oil by 20 to 38 per cent. If they are adopted, it will be necessary to raise the minimum standard for mustard oil in mustard from 0.7 to 0.9 per cent.

C. A. M.

Detection and Estimation of Neutralising Agents in Butter and Similar Products. L. W. Ferris. (*J. Ind. and Eng. Chem.*, 1920, 12, 757-760.)—Since it is not practicable to remove all the milk salts from butter, the salts in butter from neutralised cream will differ from those in butter from normal cream. On treating the sample with a known quantity of $\frac{N}{10}$ hydrochloric acid and an excess of picric acid (to precipitate proteins), and extracting the lactic acid and excess of picric acid with ether, a solution of the salts will be left. When this is titrated with sodium hydroxide solution, with methyl orange as indicator, the excess of hydrochloric acid added over the amount neutralised by the sodium hydroxide will be the alkalinity of the salts, or the amount which has combined with the bases formerly present as alkalis, lactates, and phosphates. In normal milk and milk products the alkalinity of the salts present shows a definite ratio to the inorganic phosphoric acid, being approximately 45 c.c. of $\frac{N}{10}$ -alkali solution per 1 gm. of phosphoric anhydride. In neutralised milk this ratio increases with the amount of alkali which has been used. Butter made from neutralised cream will show an alkalinity ratio similar to that of the cream from which it was made, provided that the cream, when churned, contains sufficient lactic acid to keep the phosphate in solution, otherwise the alkalinity ratio may be lower than that of the cream. About one pound of the butter is melted at 45° C., and rendered homogeneous, and the water estimated. One hundred grms. are shaken in a stoppered bottle with warm petroleum spirit until the fat has dissolved. The bottle is centrifuged, the fat solution siphoned off, and the residue shaken with 50 c.c. of $\frac{N}{10}$ hydrochloric acid and 100 c.c. of a saturated solution of picric acid continually for thirty minutes, or, at intervals, for two hours. It is then cooled and filtered, and 50 c.c. of the filtrate extracted for twenty hours with ether, after which it is transferred to an Erlenmeyer flask into which fits a tube with a double bulb with a constriction between so that the condensed vapours form a seal above the flask, while the steam is washed by the returning condensed liquid. After being gently boiled to expel all carbon dioxide the liquid is cooled and titrated with $\frac{N}{10}$ sodium hydroxide solution, with methyl orange or butter yellow as indicator. In calculating the amount of $\frac{N}{10}$ hydrochloric acid in the 50 c.c. of filtrate, the total volume of the solution is taken as 150 c.c. plus the water in the sample. The result less the $\frac{N}{10}$ alkali used in the titration gives the alkalinity of the 50 c.c. The solution is then treated with 10 c.c. of magnesia mixture and 10 c.c. of strong ammonia solution, allowed to stand over-night, and filtered. The precipitate is washed twice with 2.5 per cent. ammonia solution, and dissolved in hot dilute nitric acid, and the phosphoric anhydride is estimated volumetrically. The alkalinity as c.c. of $\frac{N}{10}$ alkali divided by the mgrms. of P_2O_5 in the 50 c.c., and multiplied by 100, gives the "alkalinity ratio." In the case of milk, butter-milk, or thin cream, 15 grms. are

taken; for thick cream, 25 grms.; for evaporated milk, 7 grms.; and for dry milk, 1 gm. Samples of neutralised cream and butter prepared from it showed alkalinity ratios ranging from 81.1 to 221.8. An approximate estimation of the acidity neutralised in butter and allied products may be made by means of the formula—

$$A = \frac{P(R - 45)}{11.11},$$

where A represents the percentage of lactic acid neutralised, P the percentage of P_2O_5 in cream or milk, and R the ratio of the sample. When this formula is applied to butter, and the amount of phosphoric anhydride in the cream from which it was made is not known, an average figure must be taken. C. A. M.

Kreis Reaction of Cottonseed Oil Products. W. B. Smith. (*J. Ind. and Eng. Chem.*, 1920, **12**, 764-766.)—The Kreis test for rancidity, in which the oil or fat is shaken with equal volumes of hydrochloric acid and phlorglucinol-ether solution, gives no coloration with fresh olive, sesame, coconut, palm, and neatsfoot oils, or with tallow or lard. Crude cottonseed oil, however, contains a chromogenic substance which gives a coloration with the reagent more pronounced than any coloration due to rancidity in other oils. Contrary to the experience of Kerr (*ANALYST*, 1918, **43**, 327), refining the oils does not always remove the reacting substance, which may also be found in certain cottonseed products. Hence the Kreis reaction is not absolutely trustworthy for the detection of rancidity in cottonseed oil. In some cases exposure to sunlight destroys the cottonseed chromogenic substance, so that oils which give a pronounced reaction before exposure may give a negative one afterwards. In this way it is sometimes possible to distinguish between rancid and non-rancid oils giving a positive Kreis reaction. C. A. M.

Method for the Estimation of Cineol in Eucalyptus Oils. T. T. Cocking. (*Pharm. J.*, 1920, **105**, 81-83.)—Three grms. of the eucalyptus oil, dried previously over calcium chloride, are mixed with 2.1 grms. of *o*-cresol, and the solidifying point of the mixture is determined. Reference to a graph constructed from the results of estimations of mixtures containing known amounts of cineol gives the quantity of cineol present in the oil under examination. Terebene may be used as the diluent for the cineol in making the standard mixtures. W. P. S.

Detection of Inorganic Phosphate in Glycerophosphates. J. L. Lizius. (*Pharm. J.*, 1920, **105**, 100-101.)—When 0.8 gm. of the glycerophosphate is mixed with 10 c.c. of dilute nitric acid and 10 c.c. of 10 per cent. ammonium molybdate solution, the presence of 0.1 per cent. or more of inorganic phosphate is indicated by the formation of a turbidity. Attention is directed to the solubility of the yellow ammonium phosphomolybdate in excess of either phosphate or glycerophosphate, and the unreliability of the test prescribed in the U.S. Pharmacopœia is possibly due to this fact. A sensitive reagent for the purpose has been described by Scott and Plimmer (*J. Physiol.*, 1906, **35**, 120); it is prepared by adding 80 c.c. of 10 per cent. ammonium molybdate solution to 12 c.c. of hydrochloric acid (sp. gr. 1.16), dissolving 20 grms. of ammonium chloride in the mixture, and then adding 10 c.c. of saturated

potassium persulphate solution. Five c.c. of this reagent are mixed with 0.1 gm. of the substance to be tested; a precipitate forms within a few minutes if the substance contains as little as 0.001 per cent. of inorganic phosphate.

W. P. S.

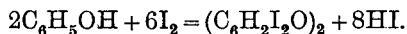
Estimation of Ipecacuanhic Acid in Ipecacuanha Preparations. R. Huerre. (*J. Pharm. Chim.*, 1920, **21**, 425-433.)—The method depends on the precipitation of ipecacuanhic acid by saturated salt solutions, ammonium sulphate giving the best results. A definite weight of ipecacuanha extract is dissolved in water, the solution treated with ammonium sulphate in quantity slightly more than is required for saturation, the precipitate is collected, and washed with saturated ammonium sulphate solution; the still moist precipitate is then dissolved on the filter in 90 per cent. alcohol, the alcoholic solution is evaporated to dryness, the residue dissolved in water, the solution filtered, and the filtrate diluted to a definite volume. An aliquot portion of this solution is evaporated to dryness, the residue of ipecacuanhic acid heated at 100° C., and weighed. An allowance must be made for the small quantity of ammonium sulphate still present; for this purpose another aliquot portion of the solution is acidified with hydrochloric acid, and the sulphate is precipitated as barium sulphate. Powdered ipecacuanha contains from 3 to 4 per cent. of ipecacuanhic acid.

W. P. S.

Assay of Opium. A. Jermstadt. (*Inaugural Dissertation, Basle, 1920*; through *Pharm. J.*, 1920, **105**, 172.)—Critical examination of official and unofficial methods for the estimation of morphine in opium showed that the lime method adopted in the British, American, French, Dutch, and other Pharmacopœias does not always give concordant results; the morphine separated is impure, but when it is freed from narcotine and calcium meconate by treatment with benzene and alcohol the results obtained are more trustworthy. The unofficial methods were found to be unsatisfactory. The following method is recommended: 6 grms. of powdered opium are mixed to a paste with 6 grms. of water, the paste is rinsed into a weighed flask, and water is added to make the contents weigh 54 grms. The mixture is shaken frequently during thirty minutes, then filtered, 40 grms. of the filtrate are mixed with 2 grms. of $\frac{N}{1}$ ammonia solution, and the mixture at once filtered. Thirty-six grms. of this filtrate are shaken with 7 grms. of ether and 4 grms. of $\frac{N}{1}$ ammonia solution for ten minutes, 10 c.c. of ether are then added, and after thirty minutes the ethereal layer is decanted through a filter; the extraction is repeated with a further 10 c.c. of ether. The contents of the flask are then poured on to the filter, the flask and filter are washed with three successive portions of 5 c.c. of water saturated with ether, and the flask and filter are dried at 100° C. The contents of the filter are then transferred to the flask, dissolved in 25 c.c. of $\frac{N}{10}$ hydrochloric acid, the solution is poured through the filter, the flask and filter are washed with about 75 c.c. of water, and the excess of acid is titrated with $\frac{N}{10}$ sodium hydroxide solution, using methyl red as indicator. Each c.c. of $\frac{N}{10}$ hydrochloric acid is equivalent to 0.0285 gm. of anhydrous morphine.

W. P. S.

Estimation of Phenol and Salicylic Acid in B.P. Ointments. G. D. Elsdon. (*Pharm. J.*, 1920, 105, 86.)—The method is an application of the iodine reaction described by Wilkie (*ANALYST*, 1911, 36, 295) :



From 0.5 to 0.6 gram. of the phenol ointment is dissolved in 5 c.c. of warm chloroform, 25 c.c. of $\frac{N}{10}$ sodium carbonate are then added, and the mixture is boiled and shaken. The shaking is continued while 25 c.c. of cold water are added; the mixture is then cooled, 25 c.c. of $\frac{N}{10}$ iodine are added, and the mixture again shaken. After five minutes the mixture is acidified slightly with sulphuric acid, and the excess of iodine is titrated with $\frac{N}{10}$ thiosulphate solution. Each c.c. of $\frac{N}{10}$ iodine solution is equivalent to 0.001568 gram. of phenol. The same procedure is adopted with salicylic acid ointments; 1 c.c. of $\frac{N}{10}$ iodine solution is equivalent to 0.002301 gram. of salicylic acid.

W. P. S.

Estimation of Phenolphthalein as Tetraiodophenolphthalein. S. Palkin. (*J. Ind. and Eng. Chem.*, 1920, 12, 766-769.)—Errors in the estimation of phenolphthalein as tetraiodophenolphthalein, due to oxidation, may be eliminated by keeping the temperature low. The alkalinity is the most important factor in the completeness of the reaction, but to obtain quantitative results it is necessary to redissolve the precipitate by means of potassium hydroxide and again precipitate it with acid, and to repeat this process several times. The phenolphthalein (not exceeding 0.25 gram.) is dissolved in the minimum quantity of potassium hydroxide solution (about 30 per cent.), and the solution chilled by the addition of 15 to 20 grms. of ice, and treated with excess of 10 per cent. iodine reagent (iodine, 10 per cent., dissolved in 15 per cent. potassium iodide solution, and the free iodine discharged with alkali). The precipitate is dissolved by potassium hydroxide solution, added drop by drop from a burette, then reprecipitated with strong acid, and this process is repeated alternately three or four times. Finally, the alkaline solution is transferred to a separating funnel, chilled with ice, treated with 0.5 c.c. of 15 per cent. sodium sulphate solution, and acidified with strong hydrochloric acid. The precipitate is extracted with 50 to 75 c.c. of a mixture of acetone and chloroform (1 : 3), the extract drawn off, and the shaking twice repeated with 35 c.c. of the mixed solvents. The extracts are washed with water in a second funnel, transferred to a tared Erlenmeyer flask, and evaporated to dryness, and the residue is dried for twenty minutes at 100° C. and weighed. The weight multiplied by 0.3871 gives the amount of phenolphthalein. Medicinal preparations of phenolphthalein which do not contain any substances forming compounds soluble in chloroform acetone may be analysed directly by this method. But in the case of preparations containing chocolate or other constituents soluble in the mixed solvents preliminary treatment is necessary. Extraction of such tablets with petroleum spirit for about two hours will remove the fat, and the residue should then be extracted for at least an hour with pure acetone, dried at 100° C., and dissolved in alkali solution, the liquid made up to 50 c.c. and filtered, and an aliquot portion of the filtrate is taken for the estimation of the phenolphthalein as described.

C. A. M.

Estimation of Starch enclosed in Cellular Tissue by Means of Ammoniacal Copper Oxide Solution. F. Kaulfersch. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1920, 39, 344-346.)—During the analysis of an anchovy paste containing starch derived from ground beans it was found that a considerable proportion of the starch was enclosed in cellular tissue, and resisted the action of diastase and hydrochloric acid. The following method was, therefore, used for the estimation: 0.5 gm. of the dry, fat-free paste was stirred for some minutes with ammoniacal copper oxide solution, the copper then removed by treatment with hydrogen sulphide, and the solution boiled to expel excess of the latter. The solution was then heated at 65° C. for six hours with the addition of diastase, filtered, boiled under a reflux condenser for three hours with the requisite quantity of hydrochloric acid, neutralised, and the copper-reducing power determined. In this way the starch content was found to be 36.4 per cent.; when the treatment with the copper solution was omitted the result was 24.3 per cent.

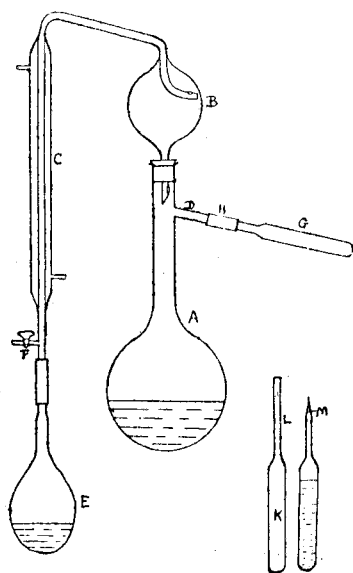
W. P. S.

Balance of the Specific Gravity of Wine. W. J. Baragiola and O. Schuppli. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1920, 39, 313-335.)—The sp. gr. of the aqueous solution of the non-alcoholic constituents of wine, as calculated from the sp. gr. of some twenty-five separate constituents, was found to be 1.0072, whilst direct determination showed the sp. gr. to be 1.0085. This difference of 0.0013 would correspond with the presence of about 3 grms. per litre of unknown or non-estimated constituents. The fact that the direct and indirect methods of estimating total solids in wine yield concordant results is probably due to the fact that the tables used in the indirect method have been compiled from the results of actual estimations.

W. P. S.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Estimation of Carbon Dioxide and Fermentable Sugars. A. Slator. (*J. Soc. Chem. Ind.*, 1920, 39, 149-151.)—The apparatus described was devised originally to estimate the total amount of carbon dioxide formed when sugars are fermented by yeast. It was subsequently found to be of general use, and can be employed in most cases where it is necessary to estimate this gas. The apparatus consists of a distillation flask, *A*, connected to a condenser, *C*, in the manner shown in the diagram. The large trap, *B*, prevents spray and froth being carried over during the distillation of carbon dioxide from *A* to the "assay" flask, *E*, which contains standard baryta water. *G* is a test-tube to which has been sealed a piece of glass tubing. This tube can be connected to the side piece, *D*, by means of pressure tubing, *H*. The whole apparatus can be exhausted through the stopcock, *F*. The estimation of carbon



dioxide in sodium carbonate is carried out in the following manner: 25 c.c. of $\frac{N}{10}$ sodium carbonate are placed in *A*, and *G* is filled with dilute sulphuric acid. Into *E* are introduced 30 c.c. of $\frac{N}{10}$ baryta water. The apparatus is exhausted, a screw clip being placed at *H* to prevent the acid in *G* passing into *A*. *F* is then closed and the clip removed. The acid in *G* is warmed and boils into *A*. Both *A* and *G* are then well boiled and *E* shaken to absorb the gas. When the distillation is complete, air free from carbon dioxide is allowed to enter the apparatus through *F*. The excess of baryta in the turbid solution in *E* is then titrated with standard hydrochloric acid, using phenolphthaleïn as indicator. The total carbonate in drinking-water can be determined by placing dilute sulphuric acid in *A*, while *G* is replaced by a funnel through which the water to be analysed is run into the exhausted apparatus; 250 c.c. of a certain water yielded CO_2 , equivalent to 14.25 c.c. of $\frac{N}{10}$ alkali. The same water showed 15.5° temporary hardness (parts CaCO_3 per 100,000) by direct titration, using methyl orange as indicator. Carbon dioxide in calcium carbonate may be estimated by distillation with phosphoric acid, while free CO_2 in liquids is determined by filling *G* with the liquid and then distilling off the CO_2 . Carbon dioxide formed in certain oxidation reactions may also be collected and estimated by means of this apparatus, an example being potassium tetroxalate. $\text{KH}_3(\text{C}_2\text{O}_4)_2, 2\text{H}_2\text{O}$ may be oxidised in the apparatus with slight excess of acidified permanganate solution. Special precautions must be observed if volatile acids other than carbonic are present, and if insoluble salts are present care must be taken to insure all the carbonate being acted upon by the acid. The estimation of sugars by alcoholic fermentation affords another opportunity for using the apparatus. Into tubes (*K*) were introduced measured quantities of solutions of pure sugars, 2 c.c. of yeast water (sp. gr. 1.017), and water to make up the volume to about 12 c.c. The tubes were plugged with cotton-wool and then sterilised. Each tube was seeded with a pure culture of yeast, the tube heated at *L*, and the glass pulled out to a fine capillary. The tube was then exhausted and sealed at *L*. Fermentation was allowed to proceed at 25° C., the tubes being shaken each day. The carbon dioxide produced was estimated in the following way: A file mark was made at *M* on the tube, which was then connected to the apparatus. After exhausting the flask and boiling the water in *A*, *F* was shut off and the end of the tube broken at *M* in the pressure tubing. The tube and flask were then both warmed and all the carbon dioxide collected in *E*. Claim, of course, is not made that the sugar is completely fermented according to the equation $\text{C}_6\text{H}_{12}\text{O}_6 = 2\text{CO}_2 + 2\text{C}_2\text{H}_5\text{OH}$. Probably about 95 per cent. of the CO_2 is produced according to this equation; another 2 per cent. comes from the auto-fermentation of the yeast, and the rest from the auto-digestion of the yeast. The apparatus was also applied in an attempt to estimate some of the constituents of ordinary brewery wort. The total amount of fermentable carbohydrates is determined by fermenting wort with yeast, filtering, and then distilling off the alcohol from a measured volume. The residue is made up again to this volume and the process repeated. From the gravity of the final residue the total amount fermented may be calculated. In a fermentation of this kind about 95 per cent. of the theoretical yield of alcohol is obtained, and in general it is found that the total amount of fermentable carbohydrates may be obtained in this manner with a fair

degree of accuracy, but it is advisable to carry out control experiments with pure sugars before using the method for any special purpose. The presence of certain enzymes in yeast serves to characterise and identify different races. The following method is recommended for carrying out such tests: For the detection of invertase, tubes containing yeast water, cane sugar (0.2 gm.), and dextrose (0.02 gm.) are inoculated with a pure culture of the yeast. The tubes are exhausted and sealed up. After about a week the carbon dioxide is distilled off and estimated. If no invertase is present in the yeast, carbon dioxide to neutralise about 4 c.c. of alkali is obtained; if present, up to 40 c.c. to 50 c.c. is neutralised. The presence of dextrose is an advantage for growth, and a certain amount of fermentation is insured. Maltose can be detected by using maltose in place of cane sugar. The presence of or absence of galactozymase can be shown by using galactose. The following results were obtained:

Yeast.	Enzyme.	Alkali Neutralised.	Presence or Absence of Enzyme.
Apiculatus	Invertase	c.c. 3	—
"	Maltase	3.7	—
Cerevisiæ	Galactozymase	31	+
Wild yeast, A	"	34	+
" " B	"	2.5	—
" " C	"	32	+

H. F. E. H.

Estimation of Volatile Acids in Fermentation Products. G. Hinard (*Ann. Chim. anal.*, 1920, 2, 239-242).—Fifty c.c. of the sample, together with 10 c.c. of water, are distilled from a flask fitted with a bulb tube connecting with a condenser; 50 c.c. of distillate are collected and titrated. Fifty c.c. of water are then added to the distillation flask, and a further 50 c.c. distilled and neutralised; these operations are repeated several times. When a curve is constructed from the results, the volumes distilled being the abscissæ and the successive quantities of alkali solution used for the neutralisations the ordinates, the asymptote of the curve indicates the volume of alkali solution necessary for the neutralisation of the total volatile acids present.

W. P. S.

Colorimetric Estimation of Glycogen. R. Thieulin. (*J. Pharm. Chim.*, 1920, 21, 91-93).—In aqueous solution glycogen gives a red-brown coloration with iodine, the intensity of the colour being proportional to the amount of glycogen, provided a small definite amount of iodine is used. To estimate glycogen in liver, the latter is treated with 60 per cent. potassium hydroxide solution, the glycogen then precipitated by the addition of an equal volume of alcohol, the precipitate is separated by centrifugal action, washed with alcohol, and dissolved in a small quantity of water (for 3 grms. of liver 10 c.c. of water will be sufficient). The

solution is neutralised with acetic acid, and 2 c.c. of it are transferred to a test-tube and treated with two drops of iodine solution (iodine, 1 gm.; potassium iodide 2 grms.; water, 20 c.c.). The coloration obtained is compared with those given by definite amounts of glycogen, each dissolved in 2 c.c. of water and treated with two drops of the iodine solution.

W. P. S.

Acidity of Ropy Milk. K. Freear and E. C. V. Venn. (*Biochem. J.*, 1920, 14, 422-431.)—The paper describes the result of work done with the organisms found in samples of ropy milk from two Lancashire farms. They were plated out upon neutral "Lemco" agar, and from both of them a Gram-positive coccus showing also diplococcal forms, and in fluid cultures short chains, was obtained. These appeared to be identical with, or closely related to, the *Streptococcus Hollandicus*, and for comparative purposes strains of this organism were also employed. The experiments show that these strains produced ropiness in milk, associated with a minimum acidity, as determined by $\frac{N}{9}$ NaOH of 0.43 per cent. lactic acid, and that the ropiness continued for varying periods of time, accompanied by an acidity which never rose above 1.0 per cent. (except on one occasion). In every case the ropiness eventually diminished, and when studied for sufficiently long periods entirely disappeared, but these changes were not accompanied by any material alteration in the acidity. The results obtained by the NaOH titration method were confirmed by electrometric determinations, from which it appeared that ropiness was found in milk with a P_H range of 5.82 to 4.10. With diminishing ropiness no appreciable alteration in the P_H value could be detected, although in one case the experiment was continued for seventeen days, by which time ropiness had disappeared.

H. F. E. H.

Mutton Bird Oil. N. Evers and H. J. Foster. (*Pharm. J.*, 1920, 105, 100.)—Two samples of oil received from Tasmania and New Zealand respectively, and stated to be mutton bird oils (*Aestrelata lessoni*), had the following physical and chemical characters:

	Sample from Tasmania.	Sample from New Zealand.
Appearance... ..	Clear brown liquid	Yellowish-brown semi-solid
Odour and taste	Slightly fishy	Fishy
Sp. gr. at 15.5°/15.5° C. ...	0.8835	0.9179 (10°/15.5° C.)
Iodine value	132	99.5
Saponification value	125.9	200
Acid value	5.7	6.8
Unsaponifiable matter	31.1 per cent.	0.98 per cent.
Ether-insoluble bromides ...	10.4 per cent.	None

The figures for the New Zealand sample raise doubts as to whether it is mutton bird oil; those for the Tasmanian sample, with the exception of the iodine value, agree with the results recorded previously by L. H. Smith (*ANALYST*, 1911, 36, 290). In any case, the oils bear little resemblance to cod-liver oil, for which they have been suggested as substitutes.

W. P. S.

Determination of Grade of Peat. G. Keppeler. (*Mitt. Ver. Förder. Moorkultur in Deuts. Reiche*, 1920 [1]; through *Chem. Zentr.*, 1920, **91**, II., 548.)—The degree of conversion to peat of mosses can be determined by decomposing the material with 72 per cent. sulphuric acid. The polysaccharides pass into solution, and the sugars can be estimated by titration with Fehling's solution. The dextrose estimated in this way, and calculated on the water- and ash-free peat, is termed the "total reduction." The maximum possible value is 68 per cent., so that if the "total reduction" for any peat be g , then $100 - g \times 100 \div 68$ is a measure of the degree of conversion of the original vegetable matter into peat. This value is called the "degree of decomposition." The degree of conversion to peat may also be estimated from the residue after treatment with 72 per cent. sulphuric acid. From this residue (referred to 100 parts of organic matter) the ash, and also the residuum left in the acid treatment of sphagnum moss (11 per cent.), are deducted in order to obtain the "degree of conversion." The newer moss peats generally show a low "degree of conversion" (scarcely 30 per cent.), whilst the older ones give a much higher value (up to 50 per cent.).

Pectins in Various Plants. A. J. W. Hornby. (*J. Soc. Chem. Ind.*, 1920, **39**, 2467.)—Examination of the substances not usually determined in the analysis of cattle foods showed that the methyl pectate content of different parts of fresh plants varied greatly when estimated by Fellenberg's method (*ANALYST*, 1918, **43**, 37). As the methyl pectate is partly decomposed on drying, the author has determined the percentage of this substance in a number of fresh food materials and in different parts of the same vegetable. It was found that a much larger proportion exists in the epidermal tissue of the roots, etc., than in the cortex, and the proportion is increased in the parts attacked by insects or otherwise mechanically injured, and also in the portions of the potato tuber exposed to light. It is suggested that this pectin has a protective effect against insect attack owing to the ease with which methyl alcohol is split off from the molecule, this alcohol acting as a strong irritant to insects. The results obtained may indicate that a methyl compound would form an efficient spray for the prevention of insect attacks, but at present the cost would be prohibitive. Tables are given showing numerous results obtained by the above method.

T. J. W.

Estimation of Urea by Means of Xanthyrol. Frenkel. (*Ann. Chim. anal.*, 1920, **2**, 234-239.)—For the estimation of urea in urine 10 c.c. of a 10 per cent. solution of the latter are acidified with 35 c.c. of glacial acetic acid, and 1 c.c. of 10 per cent. xanthyrol solution (in methyl alcohol) is added while the mixture is stirred; after ten minutes a further 1 c.c. of the reagent is added, and so on until 5 c.c. in all have been added. The precipitate formed is collected after one hour, washed with about 20 c.c. of alcohol, dried at 100° C., and weighed. The weight divided by seven gives the amount of urea. Other substances present in urine do not interfere. The method may be applied to the estimation of urea in blood, after the blood has been treated with a reagent, consisting of mercuric chloride 2.71 grms., potassium iodide 7.20 grms., glacial acetic acid 66 c.c., and water 100 c.c. The

large excess of xanthidrol required for the precipitation of urea may be recovered from the filtrate from the urea precipitate by heating the filtrate until the alcohol has been expelled, neutralising the residual solution with sodium carbonate, and adding chloroform which dissolves the xanthidrol. The chloroform solution is evaporated, and the residue of xanthidrol dissolved in methyl alcohol for further use.

W. P. S.

Nature of Yeast Fat. I. S. MacLean and E. M. Thomas. (*Biochem. J.*, 1920, 14, 483-493.)—The fat examined was obtained from the following sources: (1) Bakers' yeast supplied from the manufacturers, (2) pure culture of brewery yeast, and (3) specimens of brewery yeast. After describing the method of extraction for the fat, the authors deal with its composition. The determination of its iodine value shows that the figure varies from 121 to 175, while the saponification values show wide variation ranging from 151 to 199, depending upon the proportion of sterol present. The constituents of the yeast fat are then discussed, including an account of the fatty acids, the preparation of the methyl esters, identification of the saturated and unsaturated acids, together with an account of the preparation of sterol and its iodine value. The following conclusions were reached: (1) Palmitic, oleic, and linoleic acids have been identified with certainty in yeast fat. (2) The pentadecic acid, previously described, consists of a mixture of palmitic and lauric acids. Evidence of the presence of aluric acid has been obtained. (3) The presence of an acid melting at 77° C. has been confirmed, the m.-pt. of which agrees with that of arachidic acid. (4) No confirmation of the presence of the dodecenic acid described by Hinsberg and Roos was obtained, and the possibility of this being a mixture of lauric with oleic and linoleic acids has not yet been excluded. (5) A sterol is present partly in the free state and partly as fatty acid esters; this may constitute 20 per cent. of the total yeast fat. (6) The sterol present in yeast appears to be identical with the ergosterol isolated from ergot by Tanret. (7) The variation in m.-pt. described by different observers seems to be due to differences in the purity of the substance, but no conclusive evidence of the presence of a second sterol in yeast has yet been obtained. (8) It seems probable that the mycosterol isolated by Ikeguchi from certain fungi is also identical with ergosterol, and that ergosterol is characteristic of the whole group of cryptogams, just as cholesterol is of the animal, and phytosterol of the higher plant kingdom. (9) Yeast sterol is differentiated from the sterols of the higher plants and animals by the presence of three double bonds in its molecule.

H. F. E. H.

Zinc in the Human Organism. S. Giaya. (*J. Pharm. Chim.*, 1920, 22, 85-92.)—The results of about fifty estimations of zinc in various organs and secretions of normal human subjects are described. The organic matter was destroyed by treatment with potassium chlorate and hydrochloric acid or by means of nitric and sulphuric acid. The liquid was treated with hydrogen sulphide and filtered, the filtrate concentrated to remove excess of hydrochloric acid, diluted, and treated with ammonia in slight excess. It was then acidified with acetic acid, treated with a few c.c. of 10 per cent. sodium acetate solution, again

saturated with hydrogen sulphide, and allowed to stand for forty-eight hours. The zinc sulphide (containing a little iron) was then separated, washed with 5 per cent. acetic acid, saturated with hydrogen sulphide, and dissolved in dilute hydrochloric acid. The solution was evaporated nearly to dryness, the residue boiled with dilute hydrochloric acid and a slight excess of bromine, and the iron precipitated with ammonia. The zinc was then reprecipitated as sulphide as before, the zinc sulphide separated after forty-eight hours, washed, and dissolved in dilute hydrochloric acid, this solution again evaporated to dryness, and the residue dissolved in very dilute acetic acid. The zinc in this solution was finally estimated by titration with potassium ferrocyanide. The amounts of zinc thus found in the total viscera varied from 10 to 50 mgrms., whilst urine contained only traces (0.00017 gm. per litre). The amounts increased with the age of the subject, the viscera of an infant of three months containing only 0.009 gm. These quantities, even when they reach 0.005 gm. per 100 grms. of material, are not sufficient to interfere with toxicological examinations.

C. A. M.

ORGANIC ANALYSIS.

Colorimetric Estimation of Adrenalin. W. L. Scoville. (*J. Ind. and Eng. Chem.*, 1920, 12, 769-771.)—To 20 c.c. of water in a small flask are added 5 c.c. of 1 per cent. potassium iodate and 0.25 c.c. of $\frac{N}{1}$ hydrochloric acid. After warming to 38° C., 0.5 c.c. of standard adrenalin solution is added, and the mixture heated for fifteen minutes. To a similar mixture is added 0.5 c.c. of the (1 : 1000) solution to be tested (or an equivalent volume of a weaker solution), which is then warmed as above. After cooling, the colours of the two solutions are compared in a colorimeter. Should the colour intensities vary more than 25 per cent. it is advisable to repeat the test, using more or less of the unknown adrenalin solution.

The standard adrenalin solution should be freshly prepared by dissolving 0.05 gm. pure adrenalin in 0.5 c.c. $\frac{N}{1}$ hydrochloric acid and diluting to 50 c.c. If the solution to be compared contains bisulphite, 0.05 gm. of pure sodium bisulphite should be added to the standard solution.

A standard colour solution may also be prepared by mixing 10 c.c. of 2.5 per cent. crystallised cobalt chloride solution with 80 c.c. of water containing 2 grms. ammonium carbonate and diluting to 100 c.c. The colour of this standard closely matches that of the adrenalin solution in depths ranging from 25 to 30 mm., but with solutions containing bisulphite the results obtained are too low.

For the estimation of adrenalin in dried glands, 0.1 gm. of the gland is digested at 38° C. for half an hour in 20 c.c. of water, to which has been added 5 c.c. of the iodate solution and 0.25 c.c. of $\frac{N}{1}$ hydrochloric acid. After filtration the solution is transferred to the colorimeter and compared with the standard. From the result obtained the quantity of gland required to contain approximately 0.5 mgrm. of adrenalin may be calculated, and the estimation repeated, using this amount. The results compare very favourably with those obtained by the biological test.

T. J. W.

Rapid Volumetric Methods for the Estimation of Amino-Acids, Organic Acids, and Organic Bases. F. W. Foreman. (*Biochem. J.*, 1920, 14, 451-473.)

—*Preparation of Solution*: A known weight of the amino-acid, or its suitable salt, or of an amino-acid mixture, is dissolved in water free from CO_2 , and made up to a known volume, so that the resulting solution is approximately $\frac{N}{10}$ in strength in relation to the carboxyl-groups. In cases such as tyrosine and cystine, where the amino-acid is insoluble in water, or soluble in too large a volume of water, $\frac{N}{10}$ HCl or $\frac{N}{10}$ soda or other appropriate means must be used for bringing them into solution, so that no separation occurs on adding alcohol. When only a very small quantity of the amino-acid is available it may be weighed accurately into a suitable vessel, dissolved in the desired amount of water, and the whole of the solution used. *Stage 1, Titration in Water*: A 5 c.c. or 10 c.c. portion of the solution is titrated with aq. $\frac{N}{10}$ soda to phenolphthalein (soda standardised to phenolphthalein). *Stage 2, Titration in Alcohol*: Five c.c. or 10 c.c. of the original solution are transferred to a conical flask of about 250 c.c. capacity, ten volumes of 97 per cent. alcohol and three drops of phenolphthalein solution added, and the mixture titrated in daylight over a white plate with $\frac{N}{10}$ alcoholic potash (standardised to phenolphthalein) until a light pink colour is produced. The endpoint is usually obtained quite sharply on adding the last one or two drops of standard alkali (two drops = 0.05 c.c.). A correction is made for the original acidity of the alcohol. *Stage 3, Titration in Alcoholic Formaldehyde*: After obtaining the reading in Stage 2, the same liquid is used for Stage 3. Twelve and a half c.c. of aqueous formaldehyde solution prepared by diluting colourless formalin with two volumes of distilled water, and neutralising the mixture to phenolphthalein, are added for each 50 c.c. of alcohol used in Stage 2, and the titration continued to the same endpoint as before. A mixture of neutralised diluted formalin and alcohol in the same proportions as they have been used is then titrated, and the result obtained on completing Stage 3 is corrected accordingly. The acidity of rectified spirit is very slightly increased on adding the neutral formaldehyde solution. The result obtained in Stage 1 gives useful information when dealing with the dibasic amino-acids, arginine, and salts of amino-acids. The Stage 2 titration value includes the reading obtained in Stage 1. Several amino-acids are correctly estimated in Stage 2. The increase in titration value obtained in Stage 3 gives an idea of the character of the amino-acid, and, when dealing with an amino-acid mixture, affords an indication of the amount of dibasic amino-acids and proline present. The carboxyl-groups of all the amino-acids contained in an amino-acid mixture, except that of arginine, are estimated by the total titration value obtained on completing Stage 3. Ammonia, primary, secondary, and tertiary amines, and basic methylene derivatives of secondary amines do not form ionisable compounds with phenolphthalein in alcoholic solutions containing water, if the concentration of alcohol is sufficiently high. In aqueous alcoholic solutions of the salts of these bases the acid radicles can be titrated accurately with $\frac{N}{10}$ alkali, using phenolphthalein as indicator, if more than about 80 per cent. alcohol is present. When aqueous alcoholic solutions of certain amino-acids containing about 85 per cent. alcohol are titrated with standard alcoholic potash, the amino- or imino-groups liberated from their "internal salt" combinations resemble ammonia and the amines in showing no basicity to phenolphthalein, and the

carboxyl-groups are accurately estimated. Other amino-acids, more particularly dibasic amino-acids and proline, give low results when titrated in alcohol under these conditions, possibly owing to loose combination of alcohol with a carboxyl-group, or loose condensation. The subsequent addition of formaldehyde or acetone, however, results in a disturbance of the equilibrium, so that the carboxyl-groups titrate quantitatively. The effect of acetone upon the basicity of the basic groups of amino-acids to phenolphthalein is similar to that of alcohol. The amino-acids tested up to the present have all given practically quantitative results when titrated with $\frac{N}{10}$ alkali in aqueous acetone containing 80 to 85 per cent. acetone. It has been shown further that the method is capable of much wider application. The total acids (including the carboxyl-groups of amino-acids), whether in the free state or combined with organic bases, can be accurately estimated in alcoholic preparations made from aqueous fluids such as those which contain the products of bacterial growth. As the titration value is unaffected by the free bases their removal is unnecessary. Consequently the solutions need no heating, and there is no risk of decomposition. A rapid method for estimating volatile bases is also described.

H. F. E. H.

Rapid Estimation of Carbon. L. Lescœur. (*J. Pharm. Chim.*, 1920, 21, 267-263.)—A quantity of the substance (*e.g.*, sugar, organic acid, urine, etc.) containing .05 to .2 gm. of carbon is treated in a silver crucible with 10 grms. of a mixture of equal weights of sodium and potassium nitrates, and 25 c.c. of 2*N* sodium hydroxide solution (free from carbonate) are added; the whole mixture is evaporated to dryness and heated until fused. After cooling, the mass is dissolved in water, calcium chloride solution containing an excess of ammonium chloride is added, the precipitated calcium carbonate is collected after fifteen minutes, washed, and titrated with $\frac{N}{4}$ hydrochloric acid.

W. P. S.

Volumetric Estimation of $\beta\beta$ -Dichloroethyl Sulphide. W. F. Hollely. (*J. Chem. Soc.*, 1920, 117, 898-902.)—The usual procedure for the estimation of $\beta\beta$ -dichloroethyl sulphide in "mustard gas" is to distil a known volume of the sample under diminished pressure and to collect the fraction boiling at 125-130° C./40 mm. This product is fairly pure $\beta\beta$ -dichloroethyl sulphide, melting at about 10°, but the procedure involves personal risks, and gives no accurate figure for the absolute percentage of $\beta\beta$ -dichloroethyl sulphide, as the latter fraction also contains higher chlorinated compounds and other impurities. The following volumetric method for the estimation of dichloroethyl sulphide in "mustard gas," with or without solvents, has, therefore, been devised, depending on the fact that $\beta\beta$ -dichloroethyl sulphide forms a definite double salt with cuprous chloride, of the constitution, $[(\text{CH}_2\text{Cl.CH}_2)_2\text{S}]_2\text{Cu}_2\text{Cl}_2$. As the higher chlorinated compounds do not react with cuprous chloride, the method is applicable for the absolute estimation of $\beta\beta$ -dichloroethyl sulphide. About 1 gm. of the sample is weighed into a stoppered 100 c.c. conical flask, and to this 10 c.c. of a standardised solution of cuprous chloride in absolute alcoholic hydrogen chloride are added from a burette. The cuprous chloride solution should only be prepared immediately before use. It is best to have a 10 per cent. solution of hydrogen chloride in absolute alcohol on hand, and to dissolve 5 grms.

of pure cuprous chloride in 50 c.c. of it when required. The "mustard gas" sample readily dissolves in the alcoholic solution, and the contents of the flask are allowed to remain for ten minutes in the cold, with occasional rotation. At the end of this time the whole is gradually diluted with careful agitation and cooling in water, by the addition of 50 c.c. of a 5 per cent. aqueous sodium chloride. On total dilution the contents of the flask are well mixed by careful shaking, allowed to remain for a minute or two, and the liquid is then filtered from the precipitate through glass wool into a dry burette. The filtrate is quite clear, and the amount of copper in a known volume of it is subsequently determined in terms of c.c. of $\frac{N}{10}$ sodium thiosulphate, by the titration of iodine liberated from potassium iodide. It is impracticable to wash the double salt free from the excess of cuprous chloride, as it dissociates to some extent in contact with water. This difficulty is overcome by knowing the total volume of the 10 c.c. of standard cuprous chloride solution, plus the 50 c.c. of diluent, which is found to be 59.5 c.c. The total excess of cuprous chloride is thus readily calculated from the amount contained in the known volume of the filtrate taken for the copper estimation. Usually 30 c.c. of the filtrate are run from the burette into a 250 c.c. conical flask, and 5 c.c. of hydrogen peroxide (20 per cent. by volume) are added while cold to oxidise the copper to the cupric form. The contents of the flask are then gently boiled nearly to dryness, which operation is repeated twice after the addition of 10 c.c. of water to ensure that traces of gaseous oxidising agents are removed. The residue is diluted with 50 c.c. of water and sodium carbonate solution added to give a slight precipitate, which is redissolved by the careful addition of dilute acetic acid. A slight excess of potassium iodide is added, and the liberated iodine is titrated in the usual way with $\frac{N}{10}$ -sodium thiosulphate. Together with this, the original alcoholic cuprous chloride solution is standardised in terms of c.c. of $\frac{N}{10}$ -thiosulphate by oxidising 5 or 10 c.c. with hydrogen peroxide, and subsequently treating as already detailed. From the results of these titrations, the percentage of $\beta\beta$ -dichloroethyl sulphide is readily determined. The formula of the double salt being $[(\text{CH}_2\text{Cl}.\text{CH}_2)_2\text{S}]_2\text{Cu}_2\text{Cl}_2$, 127 grms. of copper correspond with 318 grms. of $\beta\beta$ -dichloroethyl sulphide. As 1 c.c. of $\frac{N}{10}$ -thiosulphate corresponds with 0.00635 gm. of copper, therefore 1 c.c. of $\frac{N}{10}$ -thiosulphate = 0.0159 gm. of $\beta\beta$ -dichloroethyl sulphide, the percentage of which is $\frac{(A - B) \times 0.0159 \times 100}{\text{weight of sample}}$, where A = c.c. of $\frac{N}{10}$ -thiosulphate corresponding with copper in the 10 c.c. of standard cuprous chloride solution, and B = c.c. of $\frac{N}{10}$ -thiosulphate corresponding with copper in the 59.5 c.c. of filtrate, that is, the total excess of copper.

H. F. E. H.

Preparation of Diphenylamine-Sulphuric Acid Reagent. F. Haun. (*Zeitsch. Untersuch. Nahr. Genussm.*, 1920, **39**, 355-356.)—Occasionally diphenylamine reagent prepared with sulphuric acid free from nitric acid exhibits a blue coloration; this is caused by the presence of ferric salts in the sulphuric acid. Such acid may be rendered serviceable by heating it to boiling and allowing it to cool slowly; during the heating the ferric salts are reduced to ferrous salts, which do not interfere. If a small quantity of permanganate is added to the acid previously, the course of the reduction may be followed during the heating, since the permanganate is also reduced,

and a colourless acid results. The presence of the manganese salt does not interfere with the use of the reagent for the detection of nitric acid, and it even appears to increase the sensitiveness of the test.

W. P. S.

Estimation of Halogen in Organic Compounds. F. B. Dains and R. Q. Brewster. (*J. Amer. Chem. Soc.*, 1920, **42**, 1573-1579.)—The reaction between liquid ammonia, sodium, and organic compounds leads to the formation of cyanide in the case of a few substances only (chloroform, bromoform, carbon tetrachloride, chloral and bromal hydrates, ethylidene chloride, tetrachloroethylene, acetylene tetrachloride, methyl and benzyl cyanides, and ethyl cyanoacetate); the quantity of cyanide formed is variable, and the modification adopted by Clifford (*ANALYST*, 1919, **44**, 322) for its removal in the estimation of halogen is trustworthy. Application of the method to the estimation of cyanogen in organic compounds did not meet with success.

W. P. S.

Estimation of Hydrocyanic Acid. R. L. Morris. (*Pharm. J.*, 1920, **105**, 83-85.)—Comparison of various volumetric methods for the estimation of hydrocyanic acid showed that Liebig's method for the titration of cyanides is trustworthy as applied to hydrocyanic acid, provided that an excess of sodium hydroxide is not used for the preliminary neutralisation of the acid. A modification suggested by Guerin (*ANALYST*, 1906, **31**, 27), in which the hydrocyanic acid is neutralised by borax, has the advantage that an excess of borax does not interfere. Volland's method is trustworthy, as is also that proposed by Fordos and Gelis (*Cf. Guerin, loc. cit.*). Mohr's method (titration with silver nitrate solution, using potassium chromate as indicator) has no advantage over that of Liebig. A modification of Liebig's method, proposed by Deniges, depends on the titration of the cyanide in strongly alkaline solution with silver nitrite solution, using potassium iodide as indicator; this method is accurate, and the B.P. (1914) method is based on it, but it appears that four times the quantity of potassium iodide prescribed is required.

W. P. S.

Specific Rotation of Lævulose. W. C. Vosburgh. (*J. Amer. Chem. Soc.*, 1920, **42**, 1696-1704.)—The specific rotation of lævulose at 25° C. can be expressed in terms of the per cent. by weight, p , and the concentration in grms. per 100 c.c., c , respectively, by the equations—

$$[\alpha]_{D 25^\circ} = -(88.50 + 0.145p) \text{ and}$$

$$[\alpha]_{D 25^\circ} = -(88.50 + 0.150c - 0.00086c^2).$$

These equations are based on experimental results, for the range $p = 2.6$ to $p = 18.6$, and $c = 2.5$ to $c = 20$. The temperature coefficient of the specific rotation is a function of the concentration; the relation between specific rotation and temperature for temperatures between 15° and 37° C. can be expressed as—

$$[\alpha]_{D t} = [\alpha]_{D 25^\circ} + (0.566 + 0.0028c)(t - 25).$$

W. P. S.

Determination of the Relative Strengths of some Nitrogen Bases of the Aromatic Series and of some Alkaloids. F. Arnall. (*J. Chem. Soc.*, 1920, 117, 835-839.)—The bases of the aromatic series are, on the whole, feebly basic, and are usually almost insoluble in water; the salts of these bases are, however, soluble. The author, therefore, measures the degree of hydrolysis of the hydrochlorides in aqueous solution by observing the acceleration of the rate of inversion of a solution of cane sugar by means of the polarimeter. The preparation of the hydrochlorides of many of these bases not being possible, their solutions have to be prepared with the addition of the calculated quantity of acid to the weighed base after careful purification of the latter. Equal volumes of the cane-sugar solutions (5 grms. per 100 c.c.) and the solution of the hydrochloride are brought to 55° C. in the thermostat, mixed and rapidly transferred to a jacketed polarimeter tube, care being taken to keep the temperature exactly constant; readings are taken at intervals, and the "final rotation," when the sugar was completely inverted, was read after the solution had been heated to 80° C. for fifteen minutes. The degree of hydrolysis of the hydrochloride is then deduced from the reaction velocity by comparison with the velocity found by hydrochloric acid alone. The degree of hydrolysis having been found at several dilutions, the dissociation constant of the salt, the basic constant of the base, and the relative strength of the base to aniline were then calculated. The following example of a typical case shows the results obtained:

Salt.	Dilution = V.	Degree of Hydrolysis = β at 55° C.	Dissociation Constant. $K_s = \frac{\beta^2}{(1-\beta)V^2}$
Dimethylaniline hydrochloride	4	0.0098	2.4×10^{-5}
	8	0.0133	2.3×10^{-5}
	16	0.0189	2.3×10^{-5}

The more common alkaloids, such as strychnine, brucine, cocaine, and morphine, were found to be too strongly basic to give satisfactory results by this method. Full tables are given showing the relative strengths and basic constants of twenty bases, of which the three following may be taken as representative:

RELATIVE STRENGTHS AND BASIC CONSTANTS OF THE BASES.

Base.	K_s .	$K_b = \frac{K_w}{K_s}$.	Aniline = 100.
<i>p</i> -Toluidine	4.0×10^{-5}	3.00×10^{-10}	250.00
<i>o</i> -Toluidine	1.59×10^{-4}	7.50×10^{-11}	62.00
Benzanilide	5.5×10^{-2}	2.18×10^{-13}	0.18

K_s = hydrolysis constant of the hydrochloric in aqueous solution.

K_b = basic constant.

K_w = dissociation constant for water, assumed to be equal to 1.2×10^{-14} , at 55° C.

It will be noted that all the values are relative to aniline, which is taken as 100. In another table is given the percentage degree of hydrolysis of hydrochlorides of some thirty bases, for which values the original paper should be consulted.

H. F. E. H.

Detection of Minute Quantities of Petroleum Spirit in Vegetable Oils.

M. Aida. (*J. Soc. Chem. Ind.*, 1920, **37**, 152T.)—Nastjukoff's formolite reaction (*ANALYST*, 1912, **39**, 274) may be applied successfully for the purpose as follows: The oil (50 to 100 grms.) is saponified by means of potassium hydroxide solution. Distilled water and pure calcium chloride solution are added, the liquid distilled by means of steam, and the distillate treated with 40 per cent. formaldehyde solution and a few drops of concentrated sulphuric acid. A reddish-brown film coloration on the surface of the liquid, gradually changing to deep yellow, indicates the presence of petroleum spirit. If a few drops of the distillate are added to water a brilliant interference ring of optical waves is produced on the surface of the water; this ring becomes almost invisible after standing for some time, and disappears completely on heating. With soya bean oil the ring does not change, even on heating. The above process is capable of detecting traces of petroleum spirit in vegetable oils, and may be made the basis of a quantitative method, the formolite precipitate being weighed after drying at 110° to 115° C. (see also *Proceedings Seventh Congress Applied Chemistry*, 1909, Section iv. A.1, 9-13).

H. F. E. H.

Determination of Phenol in the Presence of Certain other Phenols.

R. M. Chapin. (*J. Ind. and Eng. Chem.* 1920, **12**, 771-775.)—The methods described are based upon the red colour produced by phenol with an accurately prepared Millon's reagent which, with many other phenols, yields yellow or orange colours. The reagent is prepared by dissolving 2 c.c. of mercury in 20 c.c. of concentrated nitric acid and diluting with 35 c.c. of water when, if any basic salt separates, nitric acid is added drop by drop until clear. Ten per cent. sodium hydroxide solution is then run in slowly with thorough mixing until the precipitate first formed no longer redissolves, and finally 5 c.c. of 0.2 per cent. (by volume) nitric acid are added. This solution should not be used when more than one day old.

Four c.c. of a neutral aqueous solution of the sample containing 0.1 per cent. of total phenols are measured into each of two test tubes, and to one of them is added about one-half the quantity of phenol believed to be present, both being then diluted to 6 c.c. Five c.c. of Millon's reagent are run in, the contents mixed, and the tubes placed in a boiling water-bath for exactly thirty minutes, afterwards being cooled in a current of water for ten minutes. Five c.c. of 0.2 per cent. nitric acid free from oxides of nitrogen are added, and the volumes made up to 25 c.c. by the addition of water. After mixing and standing for ten minutes the solutions are filtered until brilliant, transferred to the colorimeter, and the intensities of colour matched. The percentage of phenol present in the sample is calculated by means of a somewhat complicated mathematical formula, for which the original paper should be consulted. Several variations of the above method are described, which apparently yield equally satisfactory results.

The method is fairly accurate, and a minimum of 0.04 mgrm. of phenol in the presence of 4 mgrm. of cresol, etc., in a volume of 4 c.c. may be determined. It is applicable to a number of commercial products after simple preliminary treatment.

T. J. W.

Rapid Method of Analysing Phenolsulphonic Acids. L. Desvergnès. (*Ann. Chim. anal.*, 1920, 2, 211-214.)—From 5 to 6 grms. of the sample are dissolved in 200 c.c. of water, heating being avoided. Ten c.c. of the solution are diluted with 25 c.c. of water, boiled for fifteen minutes with 25 c.c. of hydrochloric acid saturated with bromine, diluted with 200 c.c. of water, and filtered from the insoluble bromine compound. The sulphuric acid is precipitated with barium chloride to obtain the total sulphuric acid present. The combined sulphuric acid is estimated by titrating 10 c.c. of the solution with $\frac{N}{2}$ sodium hydroxide with methyl orange as indicator, and deducting the result as sulphuric acid from the total sulphuric acid. For the estimation of the phenol 10 c.c. of the solution are treated with 100 c.c. of water, 50 c.c. of hydrochloric acid, and 25 c.c. of a standardised solution of 4 grms. of potassium bromate and 14 grms. of potassium bromide per litre, and the flask closed and heated, with occasional shaking, for thirty minutes on the water-bath at 50° C. The contents of the flask are then diluted with 100 c.c. of water, 5 c.c. of 20 per cent. potassium iodide solution added, and the liberated iodine titrated with sodium thiosulphate. This gives the amount of bromine which has not combined with the phenol. The amount of the latter is calculated by means of the equation—

$$\text{Phenol per cent.} = \frac{(B - bn) \times 200 \times 100 \times 94}{10 \times P \times 480} = \frac{(B - bn) \times 1,175}{3 P},$$

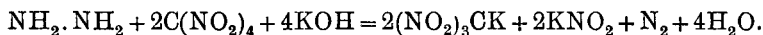
where P represents the weight of the sample, B the bromine in the 25 c.c. of bromate-bromide solution, and *b* the bromine equivalent of 1 c.c. of thiosulphate solution. The method gives accurate results with phenol sulphonic acids prepared with 93 per cent. sulphuric acid, but is less accurate when very concentrated acid is used, so that trisulphonic acid is present.

C. A. M.

Rapid Examination of Shellac, Shellac Varnish, and Lacquer. T. L. Crossley. (*J. Ind. and Eng. Chem.*, 1920, 12, 778-781.)—An approximate estimation of the amount of shellac in admixture with rosin, varnishes, etc., has been based upon the fact that the proportion of the resin insoluble in ether is fairly constant. Three samples of genuine shellac gum contained 70 to 70.2 per cent. of constituents insoluble and 28.7 to 31.8 per cent. soluble in ether, the discrepancy in one instance being probably due to oxidation. A sample of crude stick-lac gave the following results: Woody fibre, etc., 8.5; gums insoluble in ether, 70.7; and gums soluble in ether, 25.0 per cent. Mixtures of shellac and rosin in varnish examined by this method gave results agreeing closely with the manufacturers' formulæ: A weighed quantity (5 to 7 grms.) of varnish is thoroughly mixed with a large excess (50 to 60 c.c.) of ether in a tared beaker, the solution decanted through a filter into a second tared beaker, and the insoluble portion washed with successive portions of 20 c.c. of ether until the washings are practically colourless. If any deposit forms in the

filtered solution it is separated in a third beaker, and the solution is then evaporated and the residue dried and weighed. The insoluble portions in the other beakers are also dried and weighed. The total gums in the varnish are found by evaporating 5 to 10 grms. of the original varnish, and the proportion of shellac is calculated on the basis of 70 per cent. of insoluble gums in the genuine resin. C. A. M.

Effect of Reducing Agents on Tetranitromethane, and a Rapid Method of Estimation. A. Baillie, A. K. Macbeth, and N. I. Maxwell. (*J. Chem. Soc.*, 1920, 117, 880-884.)—The paper describes a study of alkaline reduction methods as applied to the estimation of tetranitromethane. These reductions result in the removal of the labile "nitroite" group with the production of salts of nitroform, which may be conveniently and safely prepared by the methods described. The procedure consisted in agitating the nitro-compound with aqueous solutions of the reducing agents containing a requisite amount of potassium hydroxide, which neutralises the nitroform produced, precipitating it as the sparingly soluble potassium salt. The solutions are thereby prevented from becoming acid, and secondary action with the reducing agent is avoided. Aqueous potassium hydroxide itself attacks tetranitromethane, with the formation of the potassium salt of nitroform, together with nitrate, nitrite, and carbonate of potassium, the quantities of which vary with concentration. The decomposition in such case, however, is much slower than when a reducing agent is present, and in the latter case the tetranitromethane is generally all converted into nitroform without the loss entailed in the formation of potassium carbonate. Results have been obtained, amongst others, with sodium sulphite, potassium sulphite, sodium potassium tartrate, and hydrazine. In all cases the nitroform salt has been identified by estimation of the percentage of potassium contained in the salt recrystallised from water; this was decomposed by sulphuric acid and the potassium weighed as sulphate. The reagent finally adopted was hydrazine from which the reaction proceeds according to the equation—



This gives results within the limits of experimental error. Half a gram of tetranitromethane is a convenient amount to use, as it liberates some 30 c.c. of nitrogen from hydrazine solutions. As the estimation is carried out in a Lunge nitrometer graduated to 0.2 c.c. the experimental error in reading the volume of gas evolved in the reaction may well be this amount. From the quantitative relation given above, 0.2 c.c. of nitrogen corresponds approximately with 0.0035 gm. of tetranitromethane. Using 0.5 gm. of the nitro-compound, the error in reading the nitrometer should theoretically be within a margin of 1 per cent. The results obtained are well within this limit. Numerous precautionary details are described and it is found that the main reaction is over in less than a minute, but further traces of nitrogen are evolved on shaking once to mix the solutions thoroughly. As the reaction is exothermic the nitrometer must be allowed to remain for some time before a volume reading is taken. Sodium hydroxide may be substituted for potash, but the latter is preferable. Conversely, standard solutions of tetranitromethane may be employed in the estimation of hydrazine in solutions of its salts. H. F. E. H.

Colorimetric Estimation of Tyrosine by the Method of Folin and Denis. R. A. Gortner and G. E. Holm. (*J. Amer. Chem. Soc.*, 1920, **42**, 1678-1692.)—Previous workers having found the above method (see *J. Biol. Chem.*, 1912, **12**, 245) unsatisfactory, the authors describe numerous experiments performed in order to determine the reliability of the results obtained by it. The method is found to be unreliable unless it is certain that no substance other than tyrosine is present which is capable of yielding a blue colour with the phenol reagent used. This reaction is also given by tryptophane, indole and its derivatives, various other substances produced by the hydrolysis of proteins, ferrous iron, and any other easily oxidised substances. Uncertainty in the results is also due to the colour development not being a linear function of the amount of reactive material present, and it is necessary to know the approximate concentration of the solution beforehand so that the maximum colour will be developed. Bone-black cannot be used for decolourising protein hydrolysates when employing this method, for not only does this material absorb tyrosine in appreciable amounts, but it yields to an acid solution some easily oxidisable substance which yields a blue colour on addition of the reagent. On the whole the method has little to recommend its adoption. T. J. W.

Detection of Water in Alcohol and other Organic Solvents. F. Henle. (*Ber.*, 1920, **53**, 719-722, through *J. Soc. Chem. Ind.*, 1920, **39**, 501A.)—A xylene solution of partially decomposed aluminium ethoxide is prepared by allowing aluminium turnings (27 grms.), absolute alcohol (276 grms.) and mercuric chloride (0.2 grms.) to react until the evolution of hydrogen subsides, and then heating the product on the water-bath until it appears dry. The alcohol of crystallisation is then distilled from an oil-bath at 210° to 220° C., and the crude aluminium ethoxide is subsequently cautiously heated until the temperature recorded by a thermometer immersed in the molten mass sinks from 340° C. to about 330° C. The product, whilst still hot, is dissolved in 500 c.c. of boiling xylene, and the solution is filtered through a dry paper; the clear, pale yellowish-brown filtrate can be preserved indefinitely if air and moisture are excluded. If a few drops of the reagent be added to a few c.c. of the liquid under examination, then, according to the quantity of water present, a voluminous, gelatinous precipitate of aluminium hydroxide is formed immediately or in the course of a few seconds. The percentage of water which can thus be detected in various solvents is as follows: ethyl alcohol, 0.05; methyl alcohol, 0.1; ether, 0.005; ethyl acetate, 0.1; acetaldehyde, 0.1; acetone, 1. The two substances last named also yield white turbidities due to the precipitation of aluminium ethoxide from the reagent, but these can be readily distinguished from aluminium hydroxide, since they immediately disappear on addition of a larger excess of reagent or of xylene.

INORGANIC ANALYSIS.

Preparation of Water free from Ammonia. G. C. Baker. (*J. Ind. and Eng. Chem.*, 1920, **12**, 798-799.)—Distilled water may be freed from ammonia (but not from nitrate, nitrite, or albuminoid nitrogen) by filtration through permutit. An automatic feeding apparatus has been devised for the purpose, consisting of a large

glass aspirator bottle containing a layer of glass beads 1.5 inches deep, covered with 12 to 14 inches of permutite. The distilled water enters the bottle at the top, and is distributed by a perforated glass bulb. It is filtered at the rate of about 1 gallon per hour, and rises from the outlet tube at the bottom through an outside tube almost to the height of the level of the water inside, and is then delivered downwards, the bent tube having an opening at the top to prevent it acting as a siphon. An overflow pipe is provided for use in flushing the filter backwards. The permutite is regenerated by passing 2 gallons of a 10 per cent. solution of common salt on to the filter, allowing it to stand overnight, and then washing the bed. It has not been determined whether the removal of the ammonia is solely a displacement of the sodium in the hydrated sodium aluminium silicate ($\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$) or whether there is also mechanical absorption of the ammonia.

C. A. M.

Electrometric Analysis of Arsenic Compounds. C. S. Robinson and O. B. Winter. (*J. Ind. and Eng. Chem.*, 1920, 12, 775-778.)—Electrometric methods of estimating arsenic are useful in the case of trivalent arsenic in coloured solutions, and for the direct estimation of pentavalent arsenic, without removal of organic matter or preliminary reduction to the trivalent condition. The apparatus described is essentially the same as that used by Hildebrand (*J. Amer. Chem. Soc.*, 1913, 35, 869), with the addition of a mechanical stirrer, and the substitution of a reflecting galvanometer for the capillary electrometer. The titrations are effected in a beaker, into which dip a platinum electrode and a calomel half-element. In estimating trivalent arsenic in, *e.g.*, London purple, 4 grms. of the sample are dissolved in hydrochloric acid below 60° C., the solution made up to 500 c.c., rendered alkaline with sodium bicarbonate, the sliding contact set to indicate the proper voltage (*e.g.*, about 260 m.v.) on the voltmeter, and the liquid mechanically stirred and titrated with $\frac{N}{10}$ iodine solution, until the completion of the oxidation is indicated on the galvanometer. For the estimation of pentavalent arsenic, the titration with hydriodic acid must be carried out in a strongly acid solution (50 per cent. by volume of sulphuric acid at the end of the titration) and at about 90° C. A special burette is used, the tip being drawn out to a capillary and bent upwards to form a hook, thus allowing the solution to be introduced at the bottom of the beaker, and to rise through the liquid before reaching the air. The reagent must not be added too rapidly, since the voltmeter reading changes slightly after the addition. Under the conditions described, good results were obtained by setting the sliding contact so that the millivoltmeter gave a reading of about 350 m.v., and titrating the solution until the galvanometer showed no movement or just reversed the direction.

C. A. M.

Iodimetric Estimation of Arsenic Acid. P. Fleury. (*J. Pharm. Chim.*, 1920, 21, 385-391.)—The arsenic acid is reduced by hydriodic acid to arsenious acid, and the latter is titrated with iodine solution. A quantity of the arsenate, equivalent to about 50 c.c. of $\frac{N}{10}$ iodine solution (*e.g.*, 0.7 gm. of sodium arsenate), is dissolved in not less than 30 c.c. of water, 1 c.c. of hydrochloric acid (sp. gr. 1.171) is added for each 10 c.c. of the solution, the mixture is heated on a boiling water-bath

for five minutes, potassium iodide is then added in quantity sufficient to make a 25 per cent. solution, the heating is continued for a further ten minutes, the mixture then cooled, and the liberated iodine eliminated by the cautious addition of dilute thiosulphate solution. An excess of sodium hydrogen carbonate is now added and the solution titrated with $\frac{N}{10}$ iodine solution. Direct titration of the iodine, liberated by the reaction, yields high results, owing to the action of atmospheric oxygen on the hydriodic acid, therefore this free iodine is destroyed by the addition of the requisite amount of thiosulphate, and the arsenious acid then estimated iodimetrically.

W. P. S.

Composition of Ancient Eastern Bronzes. M. Chikashige. (*J. Chem. Soc.*, 1920, 117, 917-922.)—The paper deals with the analysis of ancient Japanese and Chinese bronzes. The author's method in the case of corroded objects is to remove the earthy matter from a rusty article and to analyse rust and metal together. This gives, of course, too low a percentage for the metallic constituents, which should therefore be recalculated for 100. Even this method becomes doubtful where the composition of the rust has undergone change by a partial solution or disintegration before analysis. Four classes of ancient bronze mirrors were examined—namely, white, pale yellow, deep yellow, and red, according to their surface colours. These colour differences are due to the amounts of tin becoming less and less, and correspond exactly with the chronological period in which the mirrors were made. In the most recent times zinc is employed in place of tin, giving rise to the use of brass mirrors. All but the white and pale yellow had necessarily to be alloyed with mercury before use. A table summarises the analytical results obtained in the examination of sixteen specimens of Chinese, Japanese, and Corean bronze mirrors. The copper to tin ratio in most of them runs about 70 to 30, the extreme values found for copper were from 58 to 74 per cent., tin from 3.3 to 30.7 per cent., lead from 4 to 20.5 per cent.; small quantities of zinc, iron, arsenic, antimony, nickel, and, in one case, silver and gold, were also found. The presence of lead is not to be regarded as useless since it reacts with neither copper nor tin, but lies between the granules of the solid solution, acting as a cement. Without lead the mixture is apt to be too brittle to be polished. Analyses of swords, halberds, and arrow-heads are included, and numerous analyses of bell metal, money, and spoons are also recorded. Ancient Chinese coins generally contain less tin with much lead, so that they can scarcely be called bronze. Some Chinese money made between 700 and 500 B.C. contained copper running from 38 to 70 per cent., tin from 1.6 to 16 per cent., lead from 10 to 55 per cent., with the usual small quantities of antimony, iron, arsenic, and nickel. Bell metal with a high percentage of tin is sonorous, but too brittle. A Japanese bell dated about the eighth century, A.D., contained 69 per cent. copper, 15.5 per cent. tin, 5.6 per cent. lead, 8.3 per cent. antimony, 1.35 per cent. nickel, and traces of iron and arsenic.

H. F. E. H.

Volumetric Estimation of Hydrosulphides in the Presence of Sulphides, Thiosulphates, and Sulphites. A. Wöber. (*Chem. Zeit.*, 1920, 44, 601.)—Sodium hydrosulphide, when treated with an excess of mercuric chloride solution, reacts

according to the equation $2\text{NaHS} + 3\text{HgCl}_2 = 2\text{NaCl} + 2\text{HCl} + (2\text{HgS} \cdot \text{HgCl}_2)$; thio-sulphate reacts similarly, with the liberation of 2 molecules of sulphuric acid (*Cf.* Sander, *ANALYST*, 1916, **41**, 84), whilst sulphide and sulphite give neutral solutions. If a portion of the solution containing the four salts is mixed with mercuric solution and the acidity produced titrated after the addition of ammonium chloride, using methyl-orange as indicator, the acidity found is a measure of the hydrosulphide and thiosulphate content (*A*). Another portion of the solution is then treated with zinc carbonate to remove hydrosulphide and sulphide, filtered, and the thiosulphate estimated alone as just described. The difference between the acidity thus found *B*, and *A* gives that due to the hydrosulphide (*X*). To estimate sulphide and sulphite a measured quantity of the solution is added to a definite quantity of $\frac{N}{10}$ iodine solution acidified with 10 c.c. of $\frac{N}{10}$ hydrochloric acid, and the excess of iodine is titrated with $\frac{N}{10}$ thiosulphate solution; the quantity of iodine used is a measure of the sulphide, hydrosulphide, thiosulphate, and sulphite (*C*); the acidity of the mixture is then titrated with $\frac{N}{10}$ sodium hydroxide solution, using methyl-orange as indicator. Hydrosulphide and sulphite form hydriodic acid when treated with iodine according to the equations $\text{NaHS} + \text{I}_2 = \text{NaI} + \text{HI} + \text{S}$ and $\text{Na}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} = \text{Na}_2\text{SO}_4 + 2\text{HI}$. After deducting the quantity of added hydrochloric acid, the remaining acidity is due to hydrosulphide and sulphite (*D*), therefore the sulphite (*y*) is equivalent to $D - x$. The results so far obtained allow the sulphide (*z*) to be calculated by the formula $C - (2x + B/2 + y) = z$.

W. P. S.

Iodic Acid as a Characteristic Microchemical Reagent for Gaseous Ammonia. G. Denigès. (*Comptes rend.*, 1920, **171**, 177-179.)—Aqueous solutions of ammonium salts only yield crystalline precipitates with iodic acid when at least 15 to 20 per cent. of the salt is present. With gaseous ammonia, however, flat rectangular crystals of ammonium iodate, NH_4IO_3 , are immediately produced. A minute drop of a 10 per cent. solution of iodic acid, when exposed for a few seconds to ammonia vapour, becomes coated with a layer of these crystals, which may be recognised under the microscope and by their action on polarised light. The reaction is distinctive, not being given by any volatile amine, and is also very sensitive. In using it for the identification of ammonium salts in water, etc., the liquid is evaporated to about 1 c.c., and introduced, together with 0.5 grm. of calcined magnesia, into a short glass tube (3 to 4 cm. long and 15 to 16 mm. in diameter), over the mouth of which is placed an object-glass with a suspended drop of the iodic acid solution coinciding with the axis of the tube. If 1 mgrm. of ammonium salts be present, crystals will appear in a few minutes; in less than thirty minutes with 0.2 mgrm.; and in about an hour with 0.1 mgrm.

C. A. M.

Estimation of Lead in Acid Solution. N. Evers. (*Pharm. J.*, 1920, **105**, 85-86.)—In cases where it is necessary to estimate lead colorimetrically in acid solution the test and comparison solution must have the same acidity, otherwise the colorations produced by hydrogen sulphide are not comparable. By using bromophenol blue as indicator, the solutions may be brought to the colourless point of the indicator by the addition of alkali or acid (*p* then equals about 3.8); when

hydrogen sulphide solution is added, the lead coloration may be matched against that of a standard prepared in the same way. Iron does not give a coloration with hydrogen sulphide under these conditions, and the interference of copper may be prevented by the addition of cyanide; if, however, iron is present with copper, complications arise owing to the formation of ferrocyanides. It is, therefore, preferable to remove the copper by adding alum and ammonia to the solution, collecting the precipitate of aluminium hydroxide (this contains the lead, whilst the copper remains in solution), redissolving it in acid and treating the solution as described.

W. P. S.

Separation of Magnesium from Sodium and Potassium Chlorides. S. Palkin. (*J. Amer. Chem. Soc.*, 1920, **42**, 1618-1621.)—A method, described previously by the author (*ANALYST*, 1917, **42**, 54) for the separation of sodium and potassium from lithium, may be applied to the separation of the two former from magnesium, since magnesium chloride is soluble in the alcohol-ether reagent. The procedure is the same, except that 25 c.c. of absolute alcohol and 25 c.c. of ether are used for the precipitation, and that the filtrate and washings from the precipitated sodium and potassium chlorides are evaporated to dryness, and the residue dissolved in alcohol-ether mixture; a further quantity of a few mgrms. of the alkali chlorides is thus recovered. After removing the alcohol and ether from the filtrate, the magnesium may be estimated by the phosphate method.

W. P. S.

Estimation of Nickel in Steels by Direct Titration. E. H. Hall. (*J. Soc. Chem. Ind.*, 1920, **39**, 253-254r.)—The ordinary method of titrating nickel by means of potassium cyanide in a tartaric (or citric) acid solution of the steel has the drawbacks that it is difficult to observe the exact point when the final turbidity is formed, and that the excess of ammonia added is not controlled. The first drawback is obviated by transferring the tartaric acid solution of the steel, before complete neutralisation, to a measuring cylinder, which is supported over a mirror adjusted to reflect light upwards through the column of liquid. The other difficulty is obviated by taking advantage of the fact that silver chloride is soluble in ammonia solution, and that as soon as free ammonia is present any cloudiness due to the chloride will disappear. The following modification of the method gives results agreeing within the second place of decimals: The solution of 0.5 gm. of the steel in 10 c.c. of concentrated hydrochloric acid is oxidised with 2 c.c. of nitric acid on the water-bath, diluted with 35 c.c. of hot water, vigorously boiled on a hot-plate to expel nitrous fumes, and treated first with 12 c.c. of tartaric acid solution (100 grms. in 200 c.c.), and then with 8 c.c. of ammonia solution (sp. gr. 0.880). After cooling, the liquid is transferred to a Nessler cylinder holding at least 150 c.c., and about 2 c.c. of standard silver nitrate solution (2 grms. per litre) run in from a burette. The liquid is then titrated with dilute ammonia solution (sp. gr. 0.956), and stirred with a glass plunger until the turbidity due to the silver chloride disappears, this point indicating neutrality. An excess of 1 c.c. of the ammonia solution is then added, and on now adding 2 c.c. of 2 per cent. potassium iodide solution a turbidity of silver iodide is produced. Finally, the liquid is titrated with potassium cyanide solution (6.7 grms.

KCN and 1 grm. KOH per litre), a slight excess being added, and this excess titrated with the standard silver nitrate solution. In calculating the percentage of nickel the original 2 c.c. of silver nitrate solution is included. The potassium cyanide solution is best standardised upon a steel containing a known quantity of nickel.

C. A. M.

Simultaneous Precipitation of Copper and Nickel Oxides with Ferric Hydroxide. E. Torporescu. (*Comptes rend.*, 1920, 171, 303-305.)—Ferric hydroxide was precipitated in the cold by means of ammonia from solutions containing 0.2948 per cent. of ferric chloride with variable quantities of solutions of 0.3692 per cent. of copper sulphate and 0.611 per cent. of nickel chloride, and the precipitates left for three hours in contact with the liquid. The amount of copper oxide or of nickel oxide in the ignited precipitate increased with the concentration of the second salt when that of the other was kept constant. For example, the precipitates contained from 11.4 to 37.1 per cent. of copper oxide. It was not possible to free the ferric oxide completely from either copper oxide or nickel oxide by washing with ammonium nitrate or ammonia solutions, or by a second precipitation with ammonia.

C. A. M.

Estimation of Phosphoric Acid in Phosphates of Heavy Metals. F. Seeligmann. (*Chem. Zeit.*, 1920, 44, 599.)—Ten grms. of the finely powdered phosphate are mixed with about 12 grms. of sodium hydroxide solution (sp. gr. 1.075), and heated to 90° to 95° C., with continual stirring. After about fifteen minutes the solution is diluted with 3 to 4 times its volume of water, boiled, and made up to a litre. An aliquot portion is filtered, rendered slightly acid with acetic acid, and the phosphoric acid titrated with uranyl acetate in the usual way. Results in close agreement with those given by the molybdate method have been obtained with iron, zinc, and aluminium phosphates.

C. A. M.

Estimation of Potassium by the Cobaltinitrite Method. P. Wenger and C. Hémen. (*Ann. Chim. anal.*, 1920, 2, 198-199.)—Inaccuracies in the ordinary methods of estimating potassium by precipitation as sodium potassium cobaltinitrite are obviated by estimating the cobalt in the precipitate and calculating it into the corresponding proportion of potassium in the salt $\text{NaK}_2\text{CO}(\text{NO}_2)_6$. The precipitate obtained by the usual method is washed and dissolved in hydrochloric acid, and the cobalt precipitated by means of sodium hydroxide, and weighed as metallic cobalt. Or, the precipitate may be treated with sulphuric or hydrochloric acid, and the resulting solution of cobalt sulphate or chloride electrolysed. The weight of the cobalt estimated by either method, multiplied by 1.5932, gives the corresponding quantity of potassium oxide.

C. A. M.

Analysis of Sodium Silicofluoride. P. Drawe. (*Zeitsch. angew. Chem.*, 1919, 33, 312; *Chem. Zeit. Uebers.*, 1920, 44, 201.)—Commercial sodium silicofluoride, at the present time, frequently consists of mixtures of sodium silicofluoride, sodium silicate, and hydrated silicic acid. The amount of silicofluoride may be

estimated by treating 0.6 to 1 gm. of the sample with an excess of $\frac{N}{4}$ hydrochloric acid, diluting the mixture with water, and exactly neutralising the solution (to methyl orange) with $\frac{N}{4}$ potassium hydroxide solution. The neutral solution is then treated with a few drops of phenolphthalein, heated, and titrated with $\frac{N}{4}$ potassium hydroxide solution: $\text{Na}_2\text{SiF}_6 + 4\text{KOH} = 2\text{NaF} + 4\text{KF} + \text{Si}(\text{OH})_4$.

C. A. M.

Volumetric Estimation of Sulphate Ion. J. Erlich. (*Ann. Chim. anal.*, 1920, 2, 214, 215.)—The solution, which should contain about 0.01 gm. of sulphuric acid entirely in the form of an alkali salt, is exactly neutralised with sodium hydroxide or dilute hydrochloric acid, diluted to 300 to 350 c.c., boiled with an excess (about 1 gm.) of pure powdered barium carbonate, and filtered. The precipitated barium sulphate is washed three or four times with boiling water, and the alkali carbonate in the filtrate titrated with $\frac{N}{10}$ sulphuric acid.

C. A. M.

Estimation of Sulphate in Sulphonated Oils. E. J. Kern. (*J. Ind. and Eng. Chem.*, 1920, 12, 785.)—Free sulphates may be extracted from an oil by means of one extraction with 10 per cent. mono-sodium phosphate solution as completely as by three extractions in the usual way with brine and ether. In estimating the total sulphuric acid in sulphonated oils, the sample may be boiled with hydrochloric acid to decompose the oil, and the sulphate extracted with the sodium phosphate solution. A better method is to evaporate the oil with sodium carbonate, to ignite and fuse the residue, to dissolve the mass in water, and to boil the solution with sodium peroxide. The liquid is then acidified, and the sulphate precipitated with barium chloride.

C. A. M.

Analysis of Commercial Zinc. E. Olivier. (*Ann. Chim. anal.*, 1920, 2, 199-207, 226-234.)—Methods, mainly colorimetric, are described for the estimation of the commoner impurities present in commercial zinc; standard specimens containing known amounts of the impurities are used for comparison. Tin is estimated by separation as metastannic acid and as its sulphide, iron by means of thiocyanate, and lead, copper, cadmium, antimony, and arsenic are estimated by their sulphide colorations.

W. P. S.

APPARATUS, ETC.

Alundum Filtering Crucibles. D. T. Englis. (*J. Ind. and Eng. Chem.*, 1920, 12, 799.)—The difficulty of removing all soluble salts, especially from the upper edge of these crucibles, is overcome by the author as follows: The crucible containing the precipitate and fitted into a conical glass funnel by means of a rubber flange, is half filled with water, the vacuum turned on, and a smooth rubber stopper placed firmly upon the top edge of the crucible. The surrounding funnel is then filled with water, which is rapidly drawn through the upper wall of the crucible, thus washing out all soluble matter.

T. J. W.

Gas Analysis Apparatus, Accurate to 0.001 per cent., mainly designed for Respiratory Exchange Work. A. Krogh. (*Biochem. J.*, 1920, 14, 267-281.) The paper deals in a very full and elaborate manner with the experimental methods employed in gas analysis, and is fully illustrated. By employing current methods, carbon dioxide can be determined with any desired accuracy (to 0.0005 per cent.), but to obtain accurate oxygen determinations is more difficult, and even for the best instruments in actual practice errors of 0.1 per cent. are common. Since the oxygen deficit in the air leaving a respiration chamber cannot be increased beyond 2 per cent., and for many reasons should not be increased beyond 1 per cent., the accuracy obtainable is scarcely satisfactory. A great deal would be gained if the accuracy of the gas analysis could be increased sufficiently to allow an oxygen deficit of 0.5 to 1 per cent. to be analysed without causing errors exceeding 0.2 per cent., and this the author endeavours to obtain. The principal sources of error preventing the oxygen analysis being as accurate as the CO₂ determinations, are intimately connected with the presence of water and dirt in the gas burette. Water must be present to insure the saturation of the gas with vapour, since it is found impracticable to measure this completely dry, while dirt will accumulate rather rapidly from the contact of the mercury with the rubber tubing and with oxygen. The two main improvements described by the author are, firstly, the employment of three separate gas burettes, and, secondly, the raising and lowering of the mercury in the burettes by means of air pressure, thus obviating the use of rubber connections between the burettes and the reservoir. The soda or potash employed for CO₂ absorption, moreover, should never be more concentrated than 10 per cent., and must also be saturated with air; while the pyrogallate solution should be saturated with nitrogen at ordinary barometric pressure and the temperature of the bath. For absolute determinations the pyrogallate solution must also be tested with regard to its absolute absorbing power and the formation of carbon monoxide. When the potassium hydroxide used to make up the pyrogallate solution is not concentrated, very appreciable amounts of carbon monoxide are produced by the absorption of oxygen, and if a control analysis of the standard air sample shows a deviation which is outside the limits of accidental error (+0.001 per cent. for the nitrogen) the experimental analyses made on the same day should be corrected accordingly. Numerous tables are given showing the order of accuracy obtainable, and very full working details—for which the original paper must be consulted—are also described.

H. F. E. H.

Calibration, Accuracy, and Use of Gas Meters. A. Krogh. (*Biochem. J.*, 1920, 14, 282-289.)—The gas meters described are those employed in connection with respiration-chamber work, a calibration spirometer with improvements for calibrating gas meters being fully described and illustrated. The paper also deals with wet gas meters and their accurate employment, as well as dry gas meters consisting of two bellows which are alternately filled and emptied by the current of air passing through. These require no filling, and will work equally well in any position. Wet gas meters properly handled are instruments of precision. Motor-driven wet meters acting as pumps, and with a constant water level maintained by a slow current of

water, are accurate to less than 0.1 per cent. at all rates below 1 revolution per minute. When they are calibrated for more rapid rates they can be used with almost the same accuracy at rates up to 3 revolutions per minute. The volume per revolution decreases with increasing rate. In wet meters with a constant quantity of water the volume per revolution increases with increasing rate, but can be determined with equal accuracy. The subdivisions of the revolution of an experimental wet meter (Bohn meter) usually show slight errors which can be allowed for after calibration. Dry gas meters are, on the whole, less accurate than wet, and when they are arranged to show the volumes directly in litres their indications are often very inaccurate and cannot be calibrated. They should be arranged to count revolutions. Gas volumes representing fractions of a complete revolution are generally very inaccurately indicated, but the volume corresponding to a whole revolution is a practically constant quantity. Varying rates may cause variations in the volumes registered, but at practicable rates usually within 1 per cent. The calibration of a dry meter changes with age.

H. F. E. H.

Tests for Laboratory Resistance Glassware. (*J. and Proc. Inst. of Chem.*, 1920, Part III., 202-210.)—The Glass Research Committee of the Institute of Chemistry have prepared a scheme for testing laboratory glassware, with which the National Physical Laboratory have agreed generally, the object being to characterise such glassware as may safely be considered "resistance" glass. The tests, which are fully described in detail, are the minimum which such glass ought to answer, and no attempt is made to distinguish between different makes of resistance glass, nor are the tests intended to ascertain the extreme limits of resistance. For the protection of the user the described tests afford a simple means of ascertaining whether glass has any claim to be considered of resistance quality for ordinary chemical operations, while for toxicological or other special purposes the user must, of course, apply his own tests for specific purposes. The following is but a summary of the tests to be employed; for details the original must be consulted:

1. *Preliminary Treatment.*—Cleaning with boiling water, followed by 5 per cent. acetic acid.

2. *Treatment in Autoclave.*—This affords a rapid sorting test for resistance glass. The glass vessel, filled with distilled water, is heated for three hours in an autoclave at a registered pressure of 4 atmospheres. Any matter dissolved is then estimated by drying a portion of the solution for one hour at 120° C., followed by ignition (not above 650° C.) for three minutes. The result is expressed as mgrm. residue per sq. dm. The alkalinity of the rest of the water is determined by titration, using methyl orange. Express results as c.c. $\frac{N}{100}$ H₂SO₄ per square dm.

3. *Treatment with Reagents.*—Hydrochloric acid (sp. gr. 1.15) is boiled for half an hour in the vessel to be tested, the whole being enclosed in an air-bath kept at 140° C. This is repeated three times (each time with fresh acid), and finally the dissolved residue is dried down with a little ammonium carbonate, ignited, and weighed. Silica and zinc are both to be tested for in the residue; after the acid treatment the same vessel is tested by boiling in it $\frac{N}{2}$ ammonium chloride and ammonia, the dissolved matter, if any, being determined as before, all results being

expressed as mgrms. per sq. dm. Finally, $\frac{N}{2}$ sodium hydroxide is employed, the residue being tested for zinc and lead.

4. *Heat Tests—Alternative Methods.*—(a) The flask or beaker is heated in an air-oven to 120° C. for half an hour, and then instantly immersed in cold water. (b) The vessel is filled with soft paraffin wax and heated to about 155° C. and plunged in cold water; this is repeated at increasing temperatures (25° C. intervals) until it breaks. Good quality vessels will stand this treatment up to 200° C. (c) A solution of calcium chloride (sp. gr. 1.33) is boiled in the vessel for five minutes, and the whole then plunged into water at 0° C. (d) Another vessel full of water at 0° C. is plunged into boiling water.

Vessels should not crack when submitted to tests under (a), (c), and (d).

5. *Tests for Arsenic and Antimony.*—Full accounts of testing for these elements are given, with a diagram of the apparatus for distillation.

6. *Annealing.*—The vessels are examined under polarised light to detect interval stresses.

Convenient dimensions of vessels to be tested are given and the following maxima for resistance glass are recommended :

Autoclave Test.—Must not exceed 4 mgrms. per sq. dm. Alkalinity should not require more than 5 c.c. $\frac{N}{100}$ H₂SO₄ per sq. dm. The glass must not flake or peel.

Hydrochloric Acid Test on Evaporation to Dryness.—First treatment: Residue must not exceed 2 mgrms. per sq. dm. Second treatment: 1 mgrm. per sq. dm.

Ammonia and Ammonium Chloride Test.—Residue must not exceed 1.5 mgrm. per sq. dm.

H. F. E. H.

Tests for Laboratory Porcelain. (*J. and Proc. Inst. Chem.*, 1920, 210-214.)—

The tests described are those adopted by the sub-committee on porcelain of the Glass Research Committee of the Institute of Chemistry.

1. *Appearance, Shape, and Weight.*—These should at least come up to that of the porcelain in former use. The weights of vessels should not exceed pre-war average weights for articles of similar size.

2. *Tests for Porosity of Body and Imperfections in Glaze (Dye Test).*—A 0.5 per cent. solution of eosin in water answers well. Some vessels are filled and broken pieces of others immersed in the solution for eighteen hours, after which they are rinsed, dried, and examined with a hand lens. Good porcelain shows no staining at all. If the articles fail under this "dye" test, it is extremely unlikely that they will stand the remaining tests.

3. *Resistance to Heat and Sudden Changes of Temperature.*—(a) The vessels are heated by direct application of Bunsen burners, and then lifted with small, cold tongs on to cold pipeclay triangles to cool. This is repeated six times and the "dye" test again applied. (b) After thorough drying the same vessels are heated as before and cooled by being placed on cold metal (clean sheet lead). The "dye" test as before is then applied.

4. *Constancy of Weight and Resistance of Glaze to High Temperatures.*—(a) Vessels should suffer no loss of weight after heating for several hours at a good red heat and should show no tendency to stick to pipeclay, silica, or other supports. (b) The

condition of the glaze should be noted after heating for four hours at 950° C. No blistering or coaging should result.

5. *Cleaning Test.*—Cleaned, ignited, and weighed vessels should show no change in weight after immersion for twelve hours in dilute acid followed by rinsing, wiping, and ignition. Under this test, if the body is porous, liquid will have entered and on the application of sudden heat particles of glaze or porcelain will be thrown off by vapour generated from the imprisoned liquid, with resulting loss of weight.

6. *Resistance of Glaze to Acid and Alkali.*—The loss in weight sustained after prolonged treatment with boiling acid, carbonate of soda, and caustic soda should not exceed that found in comparison with high-grade pre-war porcelain.

Two simple tests for lead are finally given: (1) The porcelain is touched with hydrofluoric acid, warmed, and the acid allowed to evaporate, followed by sulphuretted hydrogen water faintly acidified with acid. (2) Fragments of the porcelain are heated to bright redness for four hours in a current of hydrogen. No darkening should ensue.

H. F. E. H.

Yellow Light in Polarimetric Determinations. L. Guglielmelli. (*Anal. Soc. Quim. Argentina*, 1918, 6, 497-499; through *J. Chem. Soc.*, 1920, 117, ii, 444.)—To obviate the drawbacks of the use of sodium chloride, Dupont proposed a mixture of salt and trisodium phosphate. This is found to work very satisfactorily. For its preparation 1 gram-molecule of disodium phosphate is dissolved in water and treated with 1 gram-molecule each of sodium hydroxide and chloride. The solution is evaporated to dryness and the residue fused.

H. F. E. H.

Testing Saccharimeters by Means of the Telescope Control Tube. C. A. Browne. (*J. Ind. and Eng. Chem.*, 1920, 12, 792-796.)—The telescope control tube consists of a metal tube which can be adjusted, by means of a screw, to give a column of solution of any length between 225 and 410 mm., the exact length at any point being indicated within 0.1 mm. by a vernier on a scale. In using the instrument to determine the errors of saccharimeter scales, due to inaccurate marking or to optical impurities in the quartz wedges, the scale of the tube itself is first calibrated, and a series of readings is made to prove that the zero point of the saccharimeter is perfectly adjusted. The control tube is then filled with a clear solution of about 25.5 grms. of sugar per 200 c.c. and placed in the trough of the saccharimeter. The temperature is maintained at about 20° C., and the polarisation closet ventilated by means of an electric fan to remove heat produced by the body of the observer. Five readings are taken successively for each scale division from the 100° point to the 95° point, and so on for every 5° to 55° point, and then back again to the 100° point. The readings are repeated with a fresh solution, and the average length of the tube for each scale division is corrected for errors in the tube scale. The corrected length, multiplied by 100 and divided by the corrected tube length for the 100° point of the saccharimeter, gives the value for that particular scale division. If, for example, the value 89.9 has been found for the 90° point, a deduction of 0.1° must be made for all readings near that point, and so on. The maximum error thus found in the

scale readings of three instruments by different makers was within the 0.05° limit fixed by the American Sugar Chemists, and the scales of commercial instruments should show this degree of accuracy. Other applications of the control tube are in comparing the scales of different saccharimeters, determining the probable error of observations of the observer, and estimating the influence of the personal equation. The general conclusion drawn from a long series of tests is that the quartz wedge saccharimeter, even in its most perfected form, has inherent defects which prevent its becoming an instrument of the highest precision.

C. A. M.



REVIEWS.

THE EXTRA PHARMACOPŒIA. By W. H. MARTINDALE, Ph.D., Ph.Ch., F.C.S., and W. W. WESTCOTT, M.B., D.P.H. Vol. I. Seventeenth Edition. 1920. H. K. Lewis and Co., Ltd., London, W.C. 1. Price 27s. net.

The appearance of a new edition of this well-known work, the first to be issued since the conclusion of the war, is very welcome. The book is necessarily of a highly technical character, but one cannot pass by the interesting Preface without wishing that a great part of it might be read by the man in the street, provided he had sufficient education to know what he was reading about. The authors would certainly not expect much appreciation from the average man, though they probably share the pious hope of the reviewer that ignorance of scientific facts may one day be a less usual attribute of Englishmen (see p. vi).

The Introduction contains useful tables and serves its purpose well; it is with the next 769 pages, wherein drugs and their uses are described, that the chief interest of the work lies. The reviewer, being a chemist, must necessarily deal principally with the chemical aspects of the book. The medical man will find data as to uses, dose, and methods of administration of the various materials, as well as remarks as to their incompatibility.

The chemist who takes an interest in *materia medica*, whether he adopts an academic or manufacturing point of view, will find a vast amount of useful information. Not merely can one find purely scientific chemical and physical data, but also many hints as to the manufacture of synthetic drugs, as well as much information relating to patents and trade-marks.

The really heroic attempt of the authors to provide "working formulæ for preparing various Organic Chemical Compounds" (Preface, pp. xvi-xviii) deserves the chemist's thanks; and the laboratory work involved in checking the "examples" of patent specifications must have entailed an enormous amount of labour. The reviewer has been able to check the advice given with regard to one or two preparations by his own results; in these cases he can fully endorse the remarks of the authors.

The treatment of certain compounds which have acquired prominence of late years calls for special mention.

Under "Acidum Hypochlorosum" we find not merely the uses of the acid itself and its salts described, but also good accounts of Chloramine—"T" and Di-Chloramine—"T"; it is hardly necessary to add that many references are given to the work of Carrel, Dakin, Watson-Cheyne, and other investigators, these antiseptics being treated in a manner which the reviewer, albeit only a chemist, found extremely interesting.

The heading "Acidum Salicylicum" covers the acid, its salts and derivatives, as well as the nearly related cresotinic acid; the 17 pages contain many references to patents and trade-marks.

"Organic Arsenic Compounds" take up 30 pages; it may be noted that the authors restrict the term "arsinic acid" to compounds of the type $R_2AsO(OH)$, whilst they refer to substances of the general formula $RAsO(OH)_2$ as "arsonic acids." On p. 204 we read:

"*Substitutes for Salvarsan* may be chemically identical, but clinically they differ remarkably." What is meant by the term "chemically identical" under such circumstances?

Twenty-five pages are devoted to "Coal-Tar Derivatives." This classification is logically weak, for here we find acriflavine, methylene-blue, phenacetin, phenazone, etc. (which are certainly derived from coal-tar), grouped together, whilst salicylic acid, equally a coal-tar derivative, has its own heading.

The account of "Colloidal Metals" occupies 21 pages; it should be pointed out that under this head colloidal solutions of various non-metals—*e.g.*, arsenic, iodine, selenium—are also described.

Other articles of considerable length are those devoted to "Hydrargyrum" (26 pages) and "Quinina" (17 pages).

A "Supplementary List of Drugs" occupies rather more than 60 pages; the reviewer feels that certain of these substances would have been better described in the main portion of the work.

The succeeding portions of the book are devoted to Vaccines and Antitoxins, Organotherapy, Poisons, and a Therapeutic Index of Diseases. As the book itself has two authors, one chemical and the other medical, so, for a complete review, it should have at least two reviewers; for an unaided specialised chemist realises his inability to deal with medical questions.

The Index, which has been tested in various ways, appears to be very complete. The printing is clear, an important matter where the use of so much small type is necessitated.

The authors are to be heartily congratulated on the appearance of this new edition.

J. T. HEWITT.

THE ANALYSIS OF DYESTUFFS AND THEIR IDENTIFICATION IN DYED AND COLOURED MATERIALS, LAKE-PIGMENTS, FOODSTUFFS, ETC. By ARTHUR G. GREEN, M.Sc., F.R.S., F.I.C. Third edition, 1920. London: Charles Griffin and Company, Ltd. Price 10s. 6d.

The first proposal for a scheme of analysis of dyestuffs was made by Witt in 1886, and this was followed by a more systematic method published by Weingärtner in 1887. In 1893 the author of this book advanced a more comprehensive scheme based on Weingärtner's system, and in the interval he has patiently carried out painstaking researches, which have culminated in a thoroughly scientific and practical programme for the detection of dyes of all classes both in substance and on the animal and vegetable fibre.

The book opens with a short but very lucid description of the hydrocarbons from which dyestuffs are derived, followed by mention of some of the more important intermediate products and an explanation of the conversion of certain of these into colouring matters. The relation between colour and chemical constitution and the meaning of "leuco" compounds are then discussed. All this is contained in 8 pages, but is by no means too short; it is exactly what the analyst or dyer requires as an introduction to the subject, and its clarity would have been obscured had its length been extended.

The classification of dyestuffs is then dealt with, both chemically and from the dyeing point of view, leading up very logically to an account of the analysis of colouring matters in substance. When it is remembered that in 1914 there were more than 200 blue dyestuffs on the market, it will readily be recognised that Professor Green is quite justified in saying that "All that can be reasonably expected of a scheme of analysis is that it should render a correct account of the dyeing and chemical relationships of the dyestuffs, and indicate in what direction the equivalent or identical products may be sought." True as this may be, yet it may be safely stated that the systematic and very practical methods of detecting dyestuffs which are expounded in this chapter should result in the identification of all but exceptionally obscure colouring matters. The important question of the detection of mixtures of dyestuffs is also adequately discussed. The paragraph on the detection of artificial dyestuffs in articles of food is of special interest to the analytical chemist. The detection of such colouring matters is described, but it appears to the reviewer that in a book entitled "Analysis of Dyestuffs" it would be very useful to find in this section exact details as to the analysis (estimation of lead, arsenic, etc.) of a selected number (say those permitted in the United States) of dyestuffs used for colouring foods.

Systematic tables, epitomising and exemplifying the principles laid down in this chapter and in the succeeding ones on the identification of dyestuffs on animal and vegetable fibres, form an important adjunct to the text.

A special chapter is devoted to the analysis of indigo, and its estimation, when dyed in conjunction with other colouring matters, is very completely described.

Now that organic dyestuffs, in the form of lakes, are so largely used instead of mineral pigments, these also have been brought into the scope of the book, accompanied by a tabular scheme of analysis.

The last chapter, a very interesting one, describes the methods employed for breaking up a dyestuff into simpler constituents in order to afford means of elucidating its constitution. Laboratory processes are given for reducing a number of azo-dyestuffs with stannous chloride or sodium hydrosulphite and identifying the products, and most of the bases and amino-acids which are commonly obtained on reduction are particularly described.

In this third edition the author has added a useful "Key to Trade Designations," based on a table prepared by Matthews (*Color Trade Journal*), which contains more than 200 trade names of groups of dyes, with their "dyeing class" and manufacturer's name; thus "Caledon" indicates vat dyes made by Scottish Dyes, Ltd.

The number of these trade names has been greatly increased of late, and the author, whilst excluding the more recent ones from the text and tables from consideration of space, has inserted the most important of them in the Index, with cross references to the products of German origin to which they are equivalent. The reviewer is inclined to agree with Professor Green in his opinion that many of these trade names are probably ephemeral, and will eventually give place to the name under which the products were known originally. Indanthrene blue, for example, has received no fewer than three new names since 1914—viz., Chloranthrene blue, Duranthrene blue, and Caledon blue—but there seems no reason, patriotic or otherwise, why the original name should not be maintained. Chemistry would indeed be reduced to chaos were this procedure applied to organic compounds to which an empirical name had first been given in Germany. It is to be hoped that dye-manufacturers may be brought to agree that only one name should be used for each dyestuff—a simple name containing an indication of the “dyeing class” and the colour, with, perhaps, a distinguishing letter or number.

In this admirable monograph, which is quite a necessity for colour chemists, dyers, and analysts, there are singularly few misprints (p. 74, “Kupenfarbstoffe” instead of Küpenfarbstoffe; p. 107, “D. R. Staebble” instead of R. Staebble; p. 110, in the formula of dinitro-*a*-naphtholsulphonic acid only one nitro-group is indicated; p. 123, “Amido-Bronner” instead of Amido-Brönner; and p. 133, “Alakli” instead of Alkali), but even after all these years the firm founded by Mr. Read Holliday of the curious Christian name is still, at the end of the Preface to the first edition, referred to as Messrs. Read, Holliday and Sons!

J. C. CAIN.

A TEXTBOOK OF QUANTITATIVE CHEMICAL ANALYSIS. By CUMMINS and KAY. 1919, Gurney and Jackson, London. Price 12s. 6d. net.

The fact that a third edition of this textbook, published originally in 1913, has been called for would indicate that it has met with general approval from students. In many respects the book is admirable, but we cannot help feeling that it fails to reach the ideal requisite for the systematic training of students in the fundamental principles of analytical chemistry. Whilst the explanations of the principles of analysis—the description of manipulative details, etc.—are clear and well put out, and cover quite elementary matter, the arrangement of the different sections of the book is confusing, and give one the impression that the authors had in a measure forgotten the real object and scope of the work. While admitting the educational value of the study of volumetric methods of analysis, we do not think that sufficient attention has been given to the systematic study of gravimetric work. The book would be much more valuable if the section dealing with gravimetric analysis was more fully dealt with, and that on systematic quantitative analysis completely rearranged. This section is arranged on alphabetical lines—a most undesirable plan; it surely would be more instructive to the student to have the elements arranged with some relation to their chemical affinities. In the section dealing with simple ores and alloys the methods described are sound and well thought out, but it is in

this section that the authors, when dealing with special technical matters, give unreliable information. As an example, under "Analysis of Superphosphate Manure," the authors make the statement that basic slag is one of the raw materials used in the manufacture of superphosphate, and apparently class all compound manures as "superphosphate." In describing the process for the determination of soluble phosphate in manures, the authors have not given correctly the official method of the Fertilisers and Feeding Stuffs Act.

Thirty pages of the text are devoted to water analysis, the excuse given for this being that students may find the determination of the small quantities of constituents normally present in water a useful exercise. We consider this a very dangerous idea—indeed, the tendency of the book is too much in the direction of training the student to specialise, and this to the sacrifice of the general principles of analytical chemistry. Although great advances have been made in the training of students at our universities and colleges, there is still much to be desired in this direction, and until analytical chemistry is fully recognised as an essential part of the study of chemistry, and not merely as a "side show," the training of chemists will be incomplete.

In more than one instance we note that in titrations the use of acid and alkali solutions of "normal" strength is indicated where very much more dilute solutions should be employed. The student is directed to read his burettes to 0.01 c.c., and to record weights to 0.1 of a milligramme. While we agree that it is very necessary to train the student to rigid accuracy in measuring and weighing, it is not desirable to lay stress on figures in the fourth place of decimals, which rarely have any significance.

E. W. VOELCKER.