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THE ANALYST

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

AN Ordinary Meeting of the Society was held on Wednesday, May 2nd, at the Chemical Society's Rooms, Burlington House. The President, Mr. P. A. Ellis Richards, F.I.C., was in the chair.

A certificate was read for the second time in favour of Mr. Robert C. Grimwood, A.I.C.

The following were elected members of the Society:—Messrs. John Myers, F.I.C., and John Loudon Buchanan, F.I.C.

The following papers were read:—"The Quantitative Estimation of Hemp and Wood in Papers containing these two Fibres," by William Dickson, F.I.C.; "The Estimation of Fat, Lactose and Moisture in Dried Milks," by H. Jephcott, M.Sc., F.I.C.; "The Estimation of Lactose by the Polarimetric and Gravimetric Methods," by A. L. Bacharach, B.A., A.I.C.; "The Melting Point and Iodine Value of Refined Natural *d*-Camphor," by Maurice S. Salamon, B.Sc.; and "The Presence of Barium and Strontium in Natural Brines," by A. G. Francis, B.Sc., F.I.C.

APPOINTMENT OF GLOUCESTERSHIRE COUNTY ANALYST.

THE Publication Committee wish it to be known that the advertisement in the May issue was inserted in ignorance of the full particulars of the appointment. Had they known the amount of work expected from the Public Analyst for the remuneration indicated, the advertisement would not have been allowed to appear.

EDITOR.

Further Notes on the Estimation of Potassium by the Perchlorate and Cobaltinitrite Methods, and on the Removal of Sulphates.

By R. LEITCH MORRIS, F.I.C.

(*Read at the Meeting, November* 1, 1922.)

A.—THE PERCHLORATE PROCESS, AND REMOVAL OF SULPHATES.

In a recent paper (ANALYST, 1920, **45**, 359) this method was shown to give extremely accurate results, even in the presence of many other bases. The previous removal of phosphate-ions, if present, is unnecessary, but sulphuric ions should always be removed, or the results may be quite erroneous, since, in the presence of salts of sodium, magnesium or other metals the sulphates of which are insoluble in alcohol, practically all the sulphate ions remain in the weighed potassium perchlorate as sulphates of these metals.

The present paper is chiefly concerned with the application of the process when calcium (or other metals the phosphates of which are insoluble in water) is present, associated with phosphoric acid; and also with the removal of the sulphate ion by a procedure that reduces the usual considerable loss of potassium in the barium sulphate precipitate to a negligible amount.

BEHAVIOUR OF PHOSPHATES AND SULPHATES IN THE PERCHLORATE PROCESS.*—In the evaporation of solutions of phosphates and sulphates with perchloric acid, assuming that complete conversion to perchlorate occurs, it is obvious that all the free phosphoric or sulphuric acid liberated remains in the residue on evaporation, since these acids are not volatile under the analytical conditions. During the evaporation, therefore, some tendency to reverse the reaction might be expected to occur, but perchloric acid is so "strong" an acid and phosphoric so "weak" that the complete conversion of almost any phosphate into perchlorate is easy. Conversion of a sulphate into a perchlorate, however, must, in general, tend to be less complete, since the "strengths" of sulphuric and perchloric acids, as measured by their conductivity numbers, are 65 and 89 respectively. In evaporating, therefore, a solution of a sulphate with perchloric acid, unless one of the products of the reaction is precipitated, there must be a tendency for the reaction to become a balanced one.

It has been previously shown that the conversion of *pure potassium sulphate* is easy if care is taken not to evaporate too far. The results for potassium are then fairly satisfactory. The reason for the complete conversion to perchlorate here is that potassium perchlorate is precipitated and removed from the sphere

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NOTE.—The percentage of perchloric acid is expressed in terms of the absolute acid ($HClO_4$).

of action; the mass activity of the perchloric acid is thus increased. With sodium sulphate, however, the products of reaction, sodium perchlorate and sulphuric acid, both remain in solution to the end of the evaporation, and the tendency for the reaction to be a balanced one must occur.

There is another important point, however, in the case of sulphates and phosphates. When the evaporated residue is treated with alcohol, if any perchlorate soluble in alcohol, such as that of sodium, is present, as soon as the soluble perchlorate begins to dissolve in the alcohol, the free phosphoric or sulphuric acid present will precipitate sodium phosphate or sulphate. Thus, in these cases, the addition of alcohol reverses the reaction; this reverse action here is slight in the case of phosphates, but is almost complete in the case of sulphates.

The results for potassium, in presence of sodium phosphate, have already been shown to be slightly too high if the evaporation with perchloric acid has been carried to dryness (as is generally preferable), but this error is easily eliminated by evaporating to a condition best described as "moist pastiness." The reason for the error is the too complete removal of the excess of perchloric acid, and the resulting slight reversal of the reaction by the action of the alcohol. A very slight excess of perchloric acid left on the residue is sufficient to prevent this.

That the addition of the alcoholic wash-liquid causes the reverse reactions just described is proved by the following qualitative experiments; *viz.* addition of phosphoric or sulphuric acid to a solution of sodium perchlorate in pure alcohol gives an immediate precipitate of sodium phosphate or sulphate respectively. However, if 0·5 per cent. perchloric acid is added to the same perchlorate solution, no precipitate is formed on adding phosphoric acid, but sulphuric acid still gives an immediate precipitate.

Although a very slight excess of perchloric acid left on the residue after evaporation with perchloric acid is sufficient to ensure accurate results for potassium, when sodium phosphate is present in the original solution, it is obvious that when the phosphate ion occurs in a solution together with the ions of the alkaline-earth and iron groups, the tendency to regenerate insoluble phosphates of these groups, on adding the alcoholic wash-liquid, will be considerably greater than if sodium phosphate alone was originally present. To prevent the potassium perchlorate retaining phosphates of calcium, magnesium, etc., a very considerable excess of perchloric acid must, in this case, be left on the residue after evaporation, as was shown by Caspari. Kreider also found that, in such cases, good results could be obtained when about thrice the amount of perchloric acid theoretically necessary to convert all the bases present into perchlorates was used.

The results given below were obtained as follows:—A solution containing potassium chloride and calcium phosphate was evaporated with 10 to 12 c.c. of 20 per cent. perchloric acid until dense fumes appeared, the residue was then dissolved in hot water, and the solution again evaporated until the appearance of dense fumes (about 1 to 2 c.c. of concentrated acid remaining), after which the residue was cooled and extracted with 15 c.c. of wash-liquid containing 97 per cent. of alcohol and 0·2 per cent. of absolute perchloric acid. After admixture, and decantation of the liquid through a tared Gooch crucible, the residue was redissolved in the dish, in hot water, a little more perchloric acid (1 to 2 c.c.) added, and the whole again evaporated to the fuming point; this residue was now extracted with 10 c.c. of wash-alcohol and transferred to the crucible, this last 10 c.c. of filtrate being used to complete the transfer; finally it was washed on the Gooch crucible with 10 to 15 c.c. of the same wash-liquid, added in small portions, and then dried at 140°–150° C.

Taken: (*a*) 0·5 grm. of calcium phosphate+0·0988 grm. of potassium chloride.
Found: 0·0991 grm. of potassium chloride. Error: +0·0003 grm.
Taken: (*b*) 0·5 grm. of calcium phosphate+0·0793 grm. of potassium chloride.
Found: (1) 0·0796 grm., (2) 0·0796 grm. of potassium chloride. Error in both cases: +0·0003 grm.

The total amount of perchloric acid used was 12 to 14 c.c., which equals rather more than 3 times the theoretical quantity. Using the same amounts of substance as in (*a*) above, and evaporating the solution only to a "moist pastiness," the potassium chloride found was 0·1030 grm.—an error of +0·0042 grm., or practically, +4 per cent. In the last case, however, it was obvious, from the behaviour of the residue on extraction with the alcohol, that something abnormal had occurred; the liquid did not clear readily on standing; the cloudiness being due to some finely divided calcium phosphate being regenerated, owing to too little perchloric acid having been left in the residue on evaporation. If this occurs, the estimation may be saved by decanting the alcoholic solution carefully on to a *small filter paper*, rejecting the alcoholic filtrate, and then washing the paper with a little boiling water to remove any traces of potassium perchlorate, allowing this solution to run into the basin containing the extracted residue, adding to this 2 to 3 c.c. more of perchloric acid, and evaporating the solution again to the fuming point. The filter paper, retaining some calcium phosphate, is rejected.

RECENT PAPERS ON THE PERCHLORATE PROCESS.—From what has already been said it is obvious that the process of Atkinson (ANALYST, 1921, **46**, 354) is practically a method for the direct estimation of potassium in presence of sulphates. This procedure is quite empirical, and the two apparently satisfactory results quoted can only have been obtained through a chance balancing of errors. On small amounts of potassium the results must be far too low to give even a rough approximation to the truth, and Watson (ANALYST, 1922, **47**, 1922) has shown that such is the case in practice.

Baxter and Rupert (*J. Amer. Chem. Soc.*, 1920, **42**, 2046; ANALYST, 1920, **45**, 462) have tested the use of methyl alcohol instead of ethyl alcohol in this process. They have found that potassium perchlorate is very much more soluble in anhydrous methyl alcohol containing perchloric acid than in a similar ethyl alcohol mixture. A mixture of 95 per cent. of absolute ethyl alcohol with 5 per cent. of absolute methyl alcohol containing 0·2 per cent. of perchloric acid, gave satisfactory results when the dry perchlorates of sodium and potassium were treated with 20 c.c. of this fluid, and the precipitate transferred and washed with a saturated solution of potassium perchlorate in the same acid-alcohol mixture. The results agreed, whether obtained at 0° or 21° C.; hence the previous recommendation of Baxter and Kobayashi (ANALYST, 1920, **45**, 238), of working at 0°, is shown to be unnecessary.

Note.—If the stronger variety of British industrial methylated spirits is used as a substitute for this mixture of alcohols, it should be dehydrated over quicklime.

The explosion recorded by Joseph and Martin (*J. Soc. Chem. Ind.*, 1920, **39**, 94) was certainly due to formation of the dangerously explosive ethyl perchlorate. There is, however, no danger in the usual estimation of potassium, and a moderate quantity, about 100 c.c., of a 0·2 per cent. perchloric acid solution in alcohol, can be evaporated to dryness with safety. These authors were estimating sodium directly in papyrus ash by evaporating the filtrate from the potassium perchlorate and finally treating the residue with sulphuric acid, and weighing it as Na_2SO_4. The explosion occurred when the alcoholic filtrate had been evaporated to low bulk, though a number of such determinations had been made safely. As they brought the substance into solution by fusing it with a large amount of *potassium* carbonate, their method is open to adverse criticism. A considerable excess of perchloric acid was probably present, and it also seems possible that the sulphuric acid required to form sodium sulphate was added, in this case, before all the perchloric acid and alcohol had been evaporated. Any addition of sulphuric acid at this point would certainly hasten esterification. The remarkable violence of the explosion closely resembled the behaviour of ethyl perchlorate, described by Roscoe and Schorlemmer (*Organic Chemistry*, Part I., 348 (1885)).

ELIMINATION OF THE SULPHATE ION IN THE ESTIMATION OF THE ALKALIS.—A comprehensive study of the barium sulphate precipitate, as obtained from the sulphates of the alkalis, has been published by E. T. Allen and J. Johnston (*J. Amer. Chem. Soc.*, 1910, **32**, 588; ANALYST, 1910, **35**, 331), and continued by Johnston and Adams (*ibid.*, 1911, **33**, 82; ANALYST, 1911, **36**, 426). Their work has established the following facts, as well as others of great importance:

The precipitation of solutions of alkali sulphates always causes occlusion of alkali salts in the barium sulphate. If the conditions usually recommended for sulphuric acid estimations (addition of the barium solution, drop by drop, to the diluted and but slightly acidified solution) are followed in this case, the occlusion is very considerable. The alkalis in such a precipitate are present chiefly as *sulphates* and, hence, notwithstanding this impurity, the barium sulphate obtained is always deficient. Also, if the sulpate is thus precipitated from an alkali sulphate solution containing a large amount of alkali chloride, the occlusion, when the same amount of alkali sulphate is used, is more than doubled; yet the deficiency of the barium sulphate is also more than doubled, and may here reach 3 per cent. The deficiency of barium sulphate is due to the fact that the *moist* precipitate contains also free sulphuric acid, retained as sodium bisulphate or potassium bisulphate, or perhaps, as Hulett and Duschak suggested, as a compound with barium sulphate; on igniting the precipitate this *free* acid is volatilised, normal alkali sulphate remaining in the precipitate. The frequently repeated statement that barium sulphate is soluble in solutions of alkali chlorides has been definitely disproved by Allen and Johnston. (Practically all metallic sulphates are occluded in the barium sulphate precipitated, that of magnesium least of all.)

From the ignited barium sulphate, water alone will extract about 80 per cent. of the total alkalis present.

Potassium and sodium are occluded to about the same extent, but, in the estimation of the alkalis, the fact that the equivalent of potassium is higher than that of sodium makes the loss of potassium in the final results considerably greater than the loss of sodium.

If the precipitation is made in a solution strongly acid with hydrochloric acid (*N* or 2 *N*), the occlusion of the alkalis is reduced very considerably. I have adopted this method in alkali estimations for the precipitation of sulphates present.

EXPERIMENTAL.—Based on the work of the last-named authors, this last method of precipitation was tried on pure ignited potassium sulphate taken in quantities of about 0·5 grm. or 1 grm., the salt being dissolved in water, 10 c.c. of hydrochloric acid (sp. gr. 1·16) added, and the volume made up to about 110 c.c. The sulphate in this solution was precipitated by pouring in rapidly 8 to 9 c.c. of 10 per cent. barium chloride solution. The concentration in hydrochloric acid (actually 3 per cent.) would be here somewhat below *N*-strength. After standing, the barium sulphate was filtered off and washed, the filtrate evaporated to dryness, and the residue taken up with water and filtered; about 4 mgrms. of barium sulphate remained here, representing the amount of this salt held in solution by 120 c.c. of 3 per cent. hydrochloric acid. The filtrate was evaporated to dryness, the residue dissolved, the solution treated with ammonium carbonate, the barium carbonate filtered off, and the filtrate evaporated to dryness. The residue was ignited, taken up again in a little water, digested with some more ammonium carbonate, the liquid filtered into a tared quartz crucible and evaporated to dryness, and the residue ignited gently to constant weight and weighed as potassium chloride.

The potassium remaining in the barium sulphate was estimated by igniting the precipitate, moistening it with hydrochloric acid, warming it, and then adding 25 c.c. of boiling water and 1 to 2 drops of dilute sulphuric acid, and warming the whole for 10 minutes, after which the liquid was decanted, the residue again digested with 20 c.c. of water, filtered off and washed once with water; the mixed filtrates were evaporated to dryness, and the residue strongly ignited and weighed as potassium sulphate; the equivalent weight of this as potassium chloride was then added to the weight of the potassium chloride previously obtained. Extreme care was taken throughout, and the results were corrected for traces of alkalis, derived from the same amounts of water and reagents, by blank estimations. Evaporations were effected in quartz dishes, and silica beakers were used for the precipitations from ammoniacal solutions.

A.

Taken: 0·5122 grm. of potassium sulphate, equivalent to 0·4383 grm. of potassium chloride.
Found: 0·4408 grm., 0·4401, 0·04384, 0·4394 grm. of potassium chloride.
Error: +0·0023 grm., +0·0018, +0·0001, +0·0011 grm. of potassium chloride.
Mean Error: +0·0014 grm. of potassium chloride.

B.

Taken: 1·0236 grm. of potassium sulphate, equivalent to 0·8836 grm. of potassium chloride.
Found: 0·8823, 0·8859 grm. of potassium chloride.
Error: −0·0013 grm., +0·0023 grm. of potassium chloride.
Mean Error: +0·0005 grm. of potassium chloride.

The amounts of barium sulphate obtained were about 0·69 grm. in A, and 1·4 grms. in B, but both these amounts of precipitate yielded practically the same *absolute* amount of potassium sulphate on extraction, averaging about 2 mgrms. only (equivalent to 1·7 mgrm. of potassium chloride), so that the slight *concentration* or *percentage* of potassium salt in the barium precipitate from A is reduced to one-half in that from B through doubling the concentration of the alkali sulphate solution. A further increase in the concentration of the hydrochloric acid in the solution before precipitation still more diminishes the occlusion.

These results show a great improvement over those of Series C in my previous paper, where the sulphate was precipitated in a volume of 250 to 300 c.c., containing 6 c.c. only of hydrochloric acid (1·16); there the loss of potassium chloride averaged 2½ per cent.

It is obvious that the method just described reduces the loss of potassium to a negligible amount, even when the potassium in the precipitate is not recovered.

GENERAL PROCEDURE SUGGESTED FOR PRECIPITATION OF SULPHATE.—The solution should be neutral and either contain 1 to 1·5 per cent. of total potassium and sodium salts, or else, if much sulphate is present, should be diluted so that not much over 2 grms. of barium sulphate is obtained from every hundred c.c. of the solution. The volume of the solution should be from 40 to 80 c.c.; hydrochloric acid, in amount equal to a ninth of the volume of the solution, is added, the whole heated to boiling, and the sulphate precipitated by pouring in 10 per cent. barium chloride solution in slight excess. After settling, the precipitate is filtered off and well washed; the filtrate may then be treated as below. The barium sulphate is ignited wet, then boiled for 10 minutes with 50 c.c. of water containing a few drops of hydrochloric, filtered off, washed once only, and this filtrate added to the main filtrate. The barium sulphate is then rejected.

If the estimation of both the alkalis is required, precipitation of the sulphate may be carried out either before or after the removal of the iron and alkaline-earth groups. In both cases the traces of barium sulphate dissolved in the acid filtrate will be eliminated in the precipitation of the groups mentioned when ammonia is added.

DIRECT ESTIMATION OF POTASSIUM.—This can be effected in the presence of excess of barium and other members of the iron and alkaline-earth groups. In this case, however, the original substance should first be ignited to expel ammonium salts, and the solution of the residue acidified, and treated with barium chloride as described. The filtrate is evaporated to dryness, the residue dissolved in a little water (containing a little hydrochloric acid to dissolve any phosphates of barium, calcium, etc., when phosphoric acid is present), the traces of barium sulphate filtered off and washed, and the filtrate and washings then evaporated with perchloric acid, as usual, preferably by electric heating, since gas causes traces of barium sulphate to remain in the potassium perchlorate weighed.

SUMMARY.—The perchlorate method is accurate, as shown in the previous paper.

In general, only sulphates and ammonium salts must be removed. With certain precautions, phosphates, even those only soluble in acids, do not interfere. The usual loss of potassium in the barium sulphate precipitate is entirely eliminated by the method described. The presence of even small amounts of sulphates will cause the results of the perchlorate method to be untrustworthy, if the sulphate ion is not removed.

The mixture of perchloric acid and alcohol used for the extraction of the residue of perchlorates should contain, at least, 97 per cent. of alcohol and 0·2 per cent. of perchloric acid after admixture; and, if care is taken to restrict the amount used in the extraction, and if the precipitate is transferred to a Gooch crucible by the use of the filtrate as already described, the washing may be completed with safety by finally washing with restricted small amounts of the same solution. The total filtrate need seldom exceed 35 c.c. of alcohol solution. However, the use of a saturated solution of potassium perchlorate in this mixture of alcohol and perchloric acid for the final washings *only* (the preliminary extraction being made with 20 c.c., at most, of the perchloric alcohol free from potassium perchlorate) is more convenient, as the saturated solution can be used to any extent. This last modification is suggested by Baxter and Kobayashi, in their second paper, and is better than the original one of Davis of using a saturated solution in pure alcohol alone.

Potassium perchlorate is not in the least hygroscopic; the sodium salt is deliquescent.

The alcohol can be recovered without danger and also at its original concentration, if *solid* sodium hydroxide is added, to slight alkalinity, before distilling.

B.—VOLUMETRIC COBALTINITRITE PROCESS.

Adie and Wood (*J. Chem. Soc.*, 1900, **77**, 1076) showed that, with definite concentrations of potassium salt and sodium cobaltinitrite reagent, a precipitate closely approximating to $K_2NaCo(NO_2)_6, H_2O$ was obtained, and found that, after boiling this with sodium hydroxide and filtering off the precipitated cobaltic hydroxide, the titration of the nitrites, in the filtrate, gave fair results for the potassium present. Under these conditions, 1 c.c. of 0·1 *N* $KMnO_4$=0·0007850 grm. of K_2O.

The modification now generally adopted is that of W. A. Drushel (*Amer. J. Science*, 1908, [4], **24**, **433**; ANALYST, 1908, **33**, 35). He shortened the process by oxidising the precipitate directly by heating it with excess of permanganate for about 5 minutes, then adding sulphuric acid and heating a little longer. The excess of permanganate was next reduced by means of standard oxalic acid in excess, and the remaining oxalic acid titrated with permanganate. Also, when the cobaltic hydroxide precipitated in the process of Adie and Wood, was filtered off and boiled with excess of oxalic acid in the presence of sulphuric acid, and the excess of oxalic titrated back with permanganate, the oxidising value of the cobaltic hydroxide in terms of permanganate was nearly one-twelfth of that required for the oxidation of the nitrites; whilst the amount of permanganate necessary in the presence of the cobalt was eleven-twelfths of that required for the oxidation of the nitrites after the removal of the cobalt. The factor used, therefore, in calculating the results from the direct titration is twelve-elevenths of that given by Adie and Wood; that is, in titrating the precipitate as described without first separating the cobalt, 1 c.c. of 0·1 *N* potassium permanganate= 0·0008564 grm. of potassium oxide.

The great tendency of the precipitate to pass through the filter on continued washing is eliminated if the solution, after the addition of the sodium cobaltinitrite, is evaporated to a pasty condition; on cooling, the residue is hard and dry. Sufficient cold water (20 to 50 c.c.) is added to dissolve the soluble salts, and, after settling, the liquid is filtered through a Gooch crucible with a fine asbestos felt; the precipitate is then transferred to the crucible and washed, preferably with a half-saturated solution of sodium chloride, until the washings are colourless. One or two more washings will remove the soluble nitrite completely. A measured excess of 0·1 *N* permanganate solution is, meantime, diluted with about 10 times its volume of boiling water, and this solution kept near boiling point.

The precipitate and felt are transferred into this and stirred up; then the crucible is also put in, since some of the precipitate sticks persistently to it. After 5 or 6 minutes the solution blackens, manganese hydroxide being precipitated. Dilute sulphuric acid is now added in amount sufficient to give, approximately, 2 c.c. of concentrated acid per 100 c.c. of the solution, and after heating for 5 minutes more, a measured excess of oxalic acid is added. The solution is stirred until the manganese hydroxide is completely dissolved, and then more permanganate is added until the permanent pink tint appears. If the solution shows a yellow colour, due to the cobaltous salt, before the end-point is reached, further dilution of the solution is necessary to keep the solution colourless until the end-point is reached.

Drushel standardised the permanganate first in the usual way against oxalic acid, but for the analytical process the titre was found by working under conditions similar to those obtaining in the titration of the precipitate, oxalic acid being again used as a standard. The two methods agreed very well, the difference seldom being greater than 0·1 to 0·2 c.c. in 25 c.c.

Working in this way, Drushel obtained good results. When pure potassium chloride equivalent to amounts of potassium oxide ranging from 1 to 47 mgrms. was used, the error varied from +0·5 mgrm. to −0·3 mgrm. of potassium oxide. When the precipitate was dried at 115° C. and weighed the results were all slightly above the theoretical, the average error being +0·4 mgrm. of potassium oxide. The method, when applied to fertilisers, gave results in close agreement with the platinum process.

Drushel extended the process to the analysis of soils and also of blood, urine and milk (*Amer. J. Science*, 1908 [4], **26**, 329, 555; ANALYST, 1908, **33**, 378).

In the titration of the precipitate in this process, trivalent cobalt is reduced to the divalent condition, and is not re-oxidised. F. H. MacDougall (*J. Amer. Chem. Soc.*, 1912, **34**, 1684; ANALYST, 1913, **38**, 81) tried the effect of direct titration of the precipitate by the addition of sulphuric acid to it, before adding the permanganate. The precipitate dissolved so slowly in the dilute sulphuric acid that no loss of nitrous acid occurred. More permanganate was required than in Drushel's process in the ratio of 12:11, and the factor calculated from the average permanganate consumption, which was fairly concordant, was found to be 0·000785 grm. for 1 c.c. 0·1 *N* permanganate solution. He states: "Under these conditions cobaltic oxide is shown to be unable to oxidise nitrites in sulphuric acid solution." Apparently unaware of the original procedure of Adie and Wood, he does not note that this last factor for potassium oxide is identical with theirs. He also points out that in Drushel's process the digestion of the precipitate in the hot diluted permanganate solution, before the addition of the acid, causes the solution to become alkaline. If MacDougall's method were generally satisfactory, it would be simpler and more rapid than the Drushel method.

EXPERIMENTAL.—Drushel's method, in my own trial analyses, has generally yielded accurate results, but occasionally erratic results were obtained. These seem to have been due to the time of digestion with the permanganate, before the acidification, being too short, especially when the excess of permanganate was slight. Considerable excess of permanganate should be used, as the titration volume must be considerable. A good excess of the oxalic acid should also be added; this hastens the solution of the manganese hydroxide. Accurate results were always obtained by extending the time of digestion, *before* acidifying, to 10 minutes; and, *after* acidifying, continuing the heating for 10 minutes longer, before adding the excess of oxalic acid.

PROCEDURE.—The potassium solution was acidified with acetic acid and evaporated to 10 c.c.; 10 to 15 c.c. of the cobaltinitrite reagent were poured in rapidly, and the whole warmed gently at first, the basin being covered with a clock-glass until effervescence ceased. The glass was washed down, removed, and the solution evaporated till the residue turned pasty, then cooled and extracted with either cold water or 10 per cent. acetic acid. After settling, the solution was decanted through a Gooch crucible, and the precipitate transferred to this and washed with 15 per cent. sodium chloride solution. The precipitate was then titrated as just described.

Porcelain basins of 600 c.c. capacity, heated on a boiling water-bath, are very suitable for these titrations, and are safer than glass beakers.

Pure, dried sodium oxalate was used as the standard substance, in 0·1 *N* and 0·2 *N* solutions, each containing 50 c.c. of sulphuric acid per litre; this addition makes the solutions keep well. Such solutions are about 2 *N* strength in sulphuric acid; hence the coefficient of expansion is fairly high. The permanganate solution was either 0·1 *N* or 0·2 *N*. To prevent heating of these solutions during the titration a large piece of cardboard, with the centre perforated, should be pushed down to the taps of the burettes.

The permanganate solution was standardised by proceeding as in the actual titration of the precipitate; this is necessary for accurate work.

For 0·1 *N* permanganate solution used from a 50 c.c. burette, the amount of potassium oxide taken should not exceed 0·025 grm., equivalent to 0·04 grm. of potassium chloride. For these smaller amounts of potassium the dilution of the solution during titration should be from 250 to 300 c.c.; for the larger amounts 500 c.c. will generally be sufficient to give colourless solutions up to the end-point.

Taken 0·0794 grm. of potassium chloride.
Found 0·0793, 0·0793, 0·0792, 0·0792, 0·0786 grm. of potassium chloride.

Taken 0·0534 grm. of potassium chloride.
Found 0·0534, 0·0533 grm. of potassium chloride.

Taken 0·0794 grm. of potassium chloride + 0·1 grm. of calcium carbonate.
Found 0·0787 grm. of potassium chloride.

Taken 0·0794 grm. of potassium chloride + 0·5 grm. of magnesium sulphate.
Found 0·0788 grm. of potassium chloride.

Evidently calcium and magnesium salts do not interfere; this confirms the work of Drushel, who also found that barium and strontium, in quantity, make the results too high.

Even traces of ammonia must be removed, either by ignition or by boiling with sodium carbonate; the latter process will also remove most of the substances that will interfere. The method is suitable for organic salts of potassium, but, if empyreumatic matters are present, these are probably best removed by ignition. The laboratory atmosphere should be free from ammonia.

One great advantage of this process is that sulphates do not interfere. For substances containing low percentages of potassium, the results are very good, but when the percentage of potassium is large, any slight errors in the titration process are considerably multiplied in the final percentage results.

Sodium Cobaltinitrite Solution.—If this is kept for about 3 months in diffused light, it will give, practically no precipitate when added to a potassium solution. If kept in the dark, it is still effective for qualitative tests after 2 years' storage. For quantitative work, however, the mixed solution should not be used after keeping more than a week, or an increased quantity of the solution must be used. Hence it is best to keep the two solutions and mix them on the day previous to use, filtering out the little potassium salt (always precipitated here) on the next day.

ADIE AND WOOD'S FORMULA.—(1) 113 grms. of cobalt acetate, $Co(C_2H_3O_2)_2$, $4H_2O$, and 100 c.c. of pure acetic acid made up to 500 c.c. with water. (2) 220 grms. of sodium nitrite, made up to 500 c.c. If cobalt nitrate is used, 130 grms. of the non-deliquesced salt and 100 c.c. of acetic acid are made up to 500 c.c. Equal volumes of these solutions are mixed, in a *capacious* beaker; after effervescence ceases, the solution is transferred to a pressure flask and the nitrogen oxides exhausted from the solution by the pump; or, a rapid current of air, *filtered from dust*, through a plug of cotton wool, may be aspirated through the solution for 15 minutes.

It should be noted that a 25 per cent. solution of *pure* sodium cobaltinite gives very untrustworthy results. The pure salt is precipitated on adding concentrated alcohol to solutions made according to the above formula.

The use of 10 to 15 c.c., in all, of the cobaltinitrite solution gives a satisfactory excess for amounts of potassium within the higher limit mentioned.

The Action of Potassium Carbonate on Lead Glass.

By H. DROOP RICHMOND, F.I.C.

It has long been a matter of common knowledge that glass is not an inert and insoluble substance, but is liable to be attacked by solutions of acid and alkali, and, indeed, is not entirely insoluble in water. The composition of the glass has, of course, a considerable influence on its solubility and the degree to which it is attacked by aqueous solutions. It is known that some kinds of glass will yield free alkali in solution to water sufficient to give a pink coloration with phenolphthalein, and that water will sometimes remove small flakes of siliceous material. It was, however, believed that apparently dry salts would not attack glass. A very hygroscopic dry substance such as caustic soda was, of course, known to attack glass, but it was easily seen that this was due to the fact that a strong solution was formed on the surface of the sodium hydroxide, and that the attack of the glass was due to the liquid phase. It has not hitherto been recognised that potassium carbonate, although an apparently dry salt, and although known to attract water, was sufficiently hygroscopic to have any appreciable action on glass, even though remaining apparently dry. The experiments detailed below indicate that it is not without appreciable action on glass.

On February 20th a sample was taken under the Sale of Food and Drugs Acts, following the purchase of an informal sample on the 4th of January. In each of these two samples appreciable amounts of arsenic and lead were found, the amount in the formal sample being 10 parts of arsenic and 80 parts of lead per million (soluble lead only being included). Immediately after the official sample was taken, a second sample was taken from the same container and forwarded to me. This was found to contain 10 parts per million of arsenic and 150 parts per million of lead, 25 parts per million being insoluble. The solution of potassium carbonate in water was turbid, and the insoluble portion consisted largely of silica, the percentage of potassium carbonate was 81·6, and there were only mere traces of chloride, sulphate, ammonia, phosphoric acid, iron and alumina, thus proving that the material was not commercial pearlash. As the records of the material supplied had been kept for many years past, and as no sample had ever contained arsenic and lead to anything like this amount, but had almost invariably shown less than the B.P. limit, which is two parts per million of arsenic and 5 parts per million of lead, the discovery of this material came as a surprise. Enquiries were made as to how the salt had been stored, and as the result of this the stock bottle containing the rest of the stock was sent back for examination. This contained about five ounces of potassium carbonate, and the loose material which would come out with ordinary shaking was removed, and a portion which adhered to the glass scraped off. In the portion shaken out 7 parts of arsenic and between two and three hundred parts of lead were found, and in the scrapings 12 parts of arsenic and 500 parts of lead per million. The bottle was then washed out, and it was seen that the inside surface had been attacked. An estimation of arsenic and lead in the glass of the bottle tested showed that it contained 0·34 per cent. of arsenic as As_4O_6 and 13·1 per cent. of lead oxide. These results afforded presumptive evidence that the arsenic and lead were derived from the bottle.

Experiments were then made with similar bottles which contained both lead and arsenic and, although sufficient length of time has not elapsed to render the results absolutely comparable with the conditions under which the potassium carbonate was stored in the shop, they have shown that a sample of potassium carbonate which contained originally less than 5 parts per million of lead had increased in a fortnight to 15 parts per million of lead, in three weeks to 35 parts per million of lead, and in nine weeks to 150 parts per million of lead. In these experiments the potassium carbonate was absorbing moisture rapidly, owing to the fact that the closure of the bottle was very imperfect, and at the end of three weeks the moisture had gone up to 20·5 per cent., and the potassium carbonate was clinging to the sides of the bottle. In another experiment, in which potassium carbonate containing only 16·6 per cent. of moisture was put in a well-closed lead glass bottle, no increase at all in the lead was noted in six weeks.

I think there is little doubt that these experiments show that potassium carbonate is sufficiently hygroscopic to attack the glass of the bottle in which it is stored, and especially if it becomes at all moist. I attribute this attack to the formation of a thin film of a very strong solution of potassium carbonate on the surface of the crystals, and, if the glass contains arsenic and lead, these will be dissolved in the film adhering to the glass, as arsenite and plumbate, and by disturbance during removal of potassium carbonate from time to time, the contaminated crystals will become mixed with the bulk, and gradually the whole bulk will contain quantities of arsenic and lead derived from the glass in varying proportions. I may mention that in the case of the sample taken under the Sale of Food and Drugs Acts the same bottle had been used to contain potassium carbonate continuously for at least 9 years, and no doubt a gradual small attack had been going on for that length of time.

The discovery that the sample of potassium carbonate contained arsenic and lead has led to the withdrawal of a very large number of bottles in which potassium carbonate was stored. The contents of these have been examined, and in a few of them quantities of arsenic and lead comparable with those in the official sample have been found, and in every one of these cases the bottles have been of the same kind as that mentioned above. In the majority of cases the potassium carbonate has not been found to contain these excessive quantities of arsenic and lead, and in these cases the shop bottle has been of soda glass.

The obvious lesson to be learned from these experiments is that potassium carbonate should not be stored in a lead glass bottle.

I have to thank Mr. J. M. Wilkie, B.Sc., F.I.C., for the bulk of the experiments on the bottles withdrawn and their contents, and Mr. G. F. Hall, M.B.E., B.Sc., A.I.C., for the bulk of the experimental work recorded in this paper, and I have to also thank Messrs. Boots Pure Drug Co., Ltd., in whose laboratories the work was carried out.

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

ESTIMATION OF ARSENIC BY THE ELECTROLYTIC METHOD.

THE following additional points should be noted in connection with the apparatus figured on page 113 of the issue of the ANALYST of March, 1923.

The inhibiting action of iron and phosphates can be obviated by using a fresh lead foil cathode for each estimation; in fact, this is to be recommended in all cases. In the examination of acid calcium phosphates containing a considerable quantity of iron salts, good results have been obtained by the following procedure:—Three-and-a-half grms. of the sample are mixed with 20 c.c. of water and 5 c.c. of concentrated sulphuric acid, and 2½ grms. of organic matter in the form of dried whole milk added. It has been found that the amount of sulphuric acid added must be sufficient to ensure the presence of 20 to 25 per cent. of free sulphuric acid in the liquid, and that the presence of organic matter is always advantageous. The mixture is placed in the porous pot, 2 c.c. of amyl alcohol added, and the apparatus filled with hydrogen from an auxiliary generator. The test is then run as already described.

The lead foil strips leading to the electrodes should be at least half an inch in width; otherwise they are liable to heat and fuse with the current employed, with consequent cracking of the glass vessel.

In cases where thick and viscous foodstuffs are being examined, the cathode may consist of a vertical strip of lead foil in place of a horizontal disc.

G. W. MONIER-WILLIAMS.

MINISTRY OF HEALTH,
WHITEHALL, S.W.1.

THE ESTIMATION OF LEAD IN ACID CALCIUM PHOSPHATE ("CREAM POWDER").

THE following method has been found useful for the estimation of lead in "cream powder" containing more than traces of iron; this may be present to the extent of 1 per cent.

Ten grms. of the sample (previously ignited in a silica dish at a low red heat if starch is present) are digested with 20 c.c. of hot concentrated hydrochloric acid, diluted with about 50 c.c. of water, the solution filtered, and the residue washed with hot water. The filtrate is treated with 0·6 c.c. of Fehling's copper solution (=0·01 grm. Cu), followed by ammonia until a slight permanent precipitate is produced. This precipitate is dissolved by the addition of 2 c.c. of concentrated hydrochloric acid, and the copper and lead are precipitated together by passing hydrogen sulphide through the warm solution. The precipitate is filtered off and washed with hydrogen sulphide water. The filter is then ignited in a silica crucible at low red heat, the ash digested with 10 c.c. of nitric acid (10 per cent. by volume), and the solution washed into a 100 c.c. flask, cooled and made up to the mark.

Ten c.c. (=1 grm. of the sample) are run into a 100 c.c. cylinder, diluted to about 50 c.c., made alkaline with ammonia, made up to 100 c.c., and treated with 1 c.c. of potassium cyanide solution, followed by 2 drops of sodium sulphide solution according to the directions in the B.P.

For the comparison 0·6 c.c. of Fehling's copper solution and 10 c.c. of dilute nitric acid are made up to 100 c.c., and 10 c.c. of this are run into the matching cylinder, diluted, made alkaline with ammonia, etc.

JAMES MILLER.

ANALYTICAL SECTION,
CO-OPERATIVE WHOLESALE SOCIETY, LTD.,
MANCHESTER.

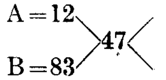
AN AVOIDANCE OF SIMULTANEOUS EQUATIONS.

IT is frequently necessary to deduce an analytical report by calculation from an experimentally determined percentage of a radicle or element common to both constituents of a mixture, such, for example, as a mixture of sodium and potassium chlorides, chlorine being estimated, or of two organic barium salts, barium being estimated.

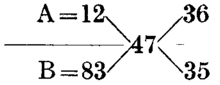
The following exceedingly simple application of the principles of alligation has been found extremely useful, and is, perhaps, worthy of record as an excellent device or method for avoiding all troublesome calculation in such cases.

Suppose compound "A" contains 12 per cent. and compound "B" contains 83 per cent. of the common radicle or element, the problem being to decide the proportions of A and B in a given mixture, found by analysis, to contain 47 per cent.

These figures are written (or simply imagined) thus:



and are always subtracted *diagonally*, the smaller being taken from the greater in every case:



It is then immediately seen that the mixture must have been 36 parts of A with 35 parts of B, and the method is equally true whatever other figures occur, no written calculation ever being required, in spite of the fact that simultaneous equations are not infrequently employed by chemists in dealing with problems of this nature.

The converse of the application is also true, and is more frequently used. Suppose one is given two solutions, say, of any substance of 12 per cent. and 83 per cent. strength respectively, it being desired to mix them in such proportions as shall produce a solution showing 47 per cent. strength.

Proceed exactly as described above, whence it will immediately be seen that 36 parts of the former with 35 parts of the latter must give the solution required (assuming no contraction or expansion occurs during mixing).

ARTHUR FAIRBOURNE.

KING'S COLLEGE, LONDON.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY BOROUGH OF SALFORD.

REPORT ON INSURANCE ACT DISPENSING.

FOR many years past "test" mixtures have been taken in the borough based upon prescriptions written on the private notepaper of medical practitioners, but no really workable scheme of direct supervision of prescriptions written on Insurance Act forms was possible until, in 1916, a clause was inserted in the terms of service for persons supplying drugs and appliances, which stated that:

> "9. All drugs and appliances shall be supplied to the person presenting such order as aforesaid free of charge to that person.
>
> "Provided nevertheless that the pharmacist shall sell to any one of the persons mentioned in section 13 of the Sale of Food and Drugs Act, 1875, or to any person authorised by such person at the price usually charged to private customers any drug or medicine prescribed or specified on the appropriate prescription form provided by the Committee for the use of insured persons and signed by an insurance practitioner."

In 1919 an agreement was reached between the Salford Insurance Committee and the Health Committee of the County Borough of Salford for the taking of samples on Insurance Act prescription forms, the procedure being based upon that ordinarily adopted under the Food and Drugs Acts.

When the scheme was first propounded a certain amount of prejudice was manifested by the Local Pharmaceutical Committee, and, to prevent misconceptions, and to give all parties an opportunity of expressing their views, a conference was arranged between the Local Pharmaceutical Association and the Administrative Departments represented by the Clerk to the Insurance Committee and the Borough Analyst.

The pharmaceutical representatives expressed fears that attempts would be made by the local officials to set up standards which were, in their opinion, unnecessary and practically impossible of attainment under ordinary dispensing conditions, and that the profession generally would be harrassed and worried by administrative details which had little or no practical importance.

It was soon found possible to allay all such fears, and the scheme as outlined was approved in principle after various reasonable safeguards desired by the pharmacists had been willingly conceded. The pharmaceutical representatives submitted that strict scientific accuracy, such as is necessary in volumetric analysis, was not essential, and that some slight departure from the true figures should be allowed without fear of legal proceedings. The following, written by Mr. Anderson and the writer in 1920, long before any of the present publicity, explains fairly well the Salford position:

> "It is, of course, readily admitted that it is not reasonable to expect exact scientific accuracy in dispensing, as it is not necessary. On the other hand, accuracy, within such limits as the limitations of the case allow, is necessary, and it becomes, therefore, a matter of great importance to decide what degree of accuracy it is reasonable to expect. In Salford it has been mutually agreed that the strength of prescriptions should not differ by more than 10 per cent. from the truth, except in such cases as sodium bicarbonate, where a leaning on the side of mercy (say 15 per cent. or thereabouts) was suggested and accepted. In the case of potent drugs, however, it was insisted that the greatest care should be taken, and that a 10 per cent. error in such cases was too great. It will be obvious that it is impossible to lay down a hard and fast rule that will cover every case, and that each case has to be decided on its own merits, but the preceding will give some idea of the frame of mind in which these things are approached."

It is very necessary to point out that these concessions were desired by the pharmacists, and that the demand for them came from their side; the writer merely acknowledged the justice of their demands. Subsequent experience has amply confirmed the writer in his original views that a prescription which does not depart from the truth to a greater amount than 10 per cent. (this allowance, of course, to include all errors due to the varying sizes of containers) does not greatly prejudice the patient. He is not concerned with pharmaceutical ethics, which may safely be left to those who are more qualified to deal with them. There is, of course, no suggestion of an agreement in the legal sense, the whole matter being merely a mutual understanding that prosecution shall not be instituted in cases where the divergence from the truth does not exceed ten per cent.

The matter of the sizes of bottles is of considerable importance to the analyst, as he does not receive the whole of the dispensed mixture, but only a portion; he consequently has to return his results as a percentage, and, where the correct amount of drug has been put into a bottle which is, say, too small, and the bottle filled up, he will find that the mixture is too strong; a bottle which is too large will, on the other hand, show an apparent deficiency of drug when the ingredients are calculated as percentages. The difficulty is overcome in Salford by the inspector submitting the original bottle to the Public Analyst along with his portion of the sample. In those cases where the bottle is not completely filled, a mark is placed on the bottle at the point to which the liquid reached. The total volume of the original mixture can then readily be ascertained, and the actual amount of drug added calculated from the composition of the sample.

The following table will show the nature of the improvement which has taken place since the first samples were taken in Salford.

Year	No. of Samples	Adulterated	Percentage of Adulteration
1914	19	8	42·1
1915	10	1	10·0
1916	14	6	42·8
1917	24	1	4·2
1918	21	4	19·0
1919	21	3	14·3
1920	31	3	9·7
1921	51	2	3·9
1922	55	3	5·4

The pharmacists have always expressed the most earnest desire to make the dispensing service as efficient as possible, and their foremost practitioners have been unremitting in their efforts to bring their erring brethren into line. Those who were merely careless have become far more careful, whilst the few really unsatisfactory members are gradually dropping out or are being removed from the panel.

G. D. Elsdon.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

FUMES FROM CHEMICAL WORKS.

R. H. Bulloch v. *Alexander Hope (jun.) & Co., Ltd.*

In this case an action was brought in Glasgow to recover damages for injury to property alleged to have been caused by chemical fumes from the defendants' works.

Sheriff Lyall, in giving judgment, said that the burden was on the pursuer to establish, first, that his property had been injuriously affected by noxious fumes; and, secondly, that these fumes emanated from the defenders' works, or, at least that these fumes so emanating had materially contributed to the injury. In his opinion, the pursuer had failed to prove the emission of fumes in sufficient quantity to do material damage. Referring to an analysis of certain leaves and pieces of metal from the pursuer's house, the Sheriff pointed out that, whilst the condition of the leaves and the rust on the metal were each attributable to the vapour of sulphuric acid, the defenders had maintained that all that was discovered was only such a condition as was found to exist in a manufacturing city like Glasgow. The pursuer's house was more than a mile from the works, and yet houses in closer proximity seemed to be immune. The cottages of the defenders' own workmen were in good condition. The pursuer, therefore, had not proved that he had suffered material injury to his property from the operations of the defenders.

COPPER SULPHATE IN TINNED PEAS.

On April 28, Messrs. Cave, Austin and Co., Ltd., were summoned at the Woolwich Police Court for the sale of tinned peas, which the analyst's certificate showed to contain copper equivalent to 3·36 grains of copper sulphate per lb., the prosecution alleging that the mixture of this amount of copper with the peas rendered them injurious to health.

Dr. Macmillan, M.O.H. for Woolwich, stated that copper sulphate, which was not a natural constituent of peas, acted as an astringent, and inhibited the action of the gastric and intestinal juices, and was, he considered, injurious to health. He admitted that he was not aware of anyone suffering ill-effects from eating peas containing the proportion of copper mentioned in the summons.

For the defence, Dr. P. A. Panton, of the London Hospital, described an experiment which he had made. He had taken peas containing just under 2 grains of copper to the lb., and, after washing them, had added to them a gastric juice, the strength of which was double the normal strength of human gastric juice. The peas were kept at body temperature for 18 hours in an incubator, this period being nine times as long as they would remain in the human body. During that time they were rotated occasionally to imitate, as far as possible, the action of the stomach. At the end of 18 hours the liquid portion was strained off the pea residue, and both residue and liquid were tested for copper. In the liquid only a trace of copper was found, the bulk of the chemical being in the pea residue. The residue was next subjected to the action of trypsin, and, after further incubation, the residue and the fluid were again separated. The liquid gave no reaction for copper, but the residue gave a strong copper reaction. Dr. Panton said that his conclusions were that, whilst a certain amount of copper was dissolved in the gastric juice, and in the preliminary washing of the peas, the bulk of the copper remained indissolubly bound up in the peas and passed out of the body undigested. It was, he said, safe to say that 60 per cent. of the copper passed out of the body, and on this account he was prepared to say that the amount of copper found on the peas under notice would not be injurious. The person would have to be on the brink of death before such a dose had any effect, and the amount shown in the analysis would not be injurious to a person in health.

The magistrate said that he had heard on one side the statement of a medical man who had experimented in the matter, and on the other the statement of one who had not; he was unable to convict, and the summons would be dismissed.

Parliamentary Notes.

HOUSE OF COMMONS.

APRIL 8.

SALE OF DISINFECTANTS.—In reply to a question by Mr. Becker, the Minister of Health (Mr. Neville Chamberlain) replied that he had no evidence to show that disinfectants totally devoid of bactericidal action were being sold to the public, but that he was aware that, judged by certain tests, the disinfectants which were on sale might differ considerably in their bactericidal power. As at present advised, he did not propose to adopt the suggestion that disinfectants so sold and described must comply with a test similar to the one required for the Army and Navy and other Government departments. He understood that advice as to the choice of disinfectants for particular purposes could generally be obtained from the health officers of local authorities.

BACTERIOLOGICAL EXAMINATION OF MILK.—The Minister of Health was asked by Sir J. Remnant whether his attention had been drawn to the representations of the Society of Medical Officers of Health and others relative to the inadequate charges for the bacteriological examination of the various grades of milk under Statutory Orders, No. 1332 (ANALYST, 1923, 27), and Circulars No. 335 and 356 (ANALYST, 1923, 25), necessitating, as it did, the services of a skilled bacteriologist and the provision of material; and would he enquire into this.

In reply, Mr. Neville Chamberlain said that he had had representations as to the fee proposed for the examination of samples of milk required under the Orders referred to in the question. He was advised that the work in question was of a routine character, and that the cost per sample should not exceed the amount which had been suggested, where arrangements were made at a laboratory for dealing with the considerable volume of samples which might be expected to result from the scheme of milk grading.

MAY 9.

PRESERVATIVES IN FOOD.—The Minister of Health announced, in reply to a question, that he had already taken preliminary steps to appoint a small Committee to enquire into the general question of the use of preservatives and colouring matters in food. This decision has been taken as the result of representations on the increasing adulteration of food with boric acid and other preservatives which have recently been made by the Medical Officer of Health for Paddington and others (*cf.* ANALYST, 1923, 216).

The Institute of Metals.

STRUCTURE OF ALLOYS.

THE thirteenth annual May lecture of the Institute of Metals was delivered on Wednesday, May 2, by Dr. W. Rosenhain, F.R.S., of the National Physical Laboratory.

Referring to the great accumulation of facts in regard to the properties and microstructure of alloys which have been forthcoming in recent years, the lecturer said that the time had arrived when it was most desirable that there should be found a key to this maze of knowledge in the form of a general theory that would link together the mass of facts into a homogeneous whole. Such a theory he attempted to put forward, basing it upon the intimate knowledge of crystal structure which had recently been acquired by means of the application of X-rays to the study of the arrangement of atoms in crystals.

The crystal structures found in pure metals became modified in the case of alloys, particularly in those called solid solutions, where a second kind of atom, the atom of the alloying element, entered into the structure of the crystal and produced in it certain minute changes. With regard to such changes the lecturer put forward two simple principles and was then able to show a striking series of inferences from his theory, which accorded closely with a large number of experimental facts.

Connections between various series of properties in metals and their alloys were established which had not formerly been recognised, such as the relation between hardness and alloying power. Especially important was the connection between the minute distortion of crystal structure which occurred in alloys and their behaviour on melting and freezing, while such phenomena as plasticity, diffusion and others fell easily into line with the same type of explanation.

Most important of all, perhaps, was the fact that this new theory of alloy structure afforded a ready explanation of the electrical properties of metals and alloys and the changes of those properties when the metal was heated or cooled. These explanations covered the mysterious phenomena of super-conductivity found in many metals when cooled nearly to the absolute zero of temperature.

Bureau of Physico-Chemical Standards.

THIRD ANNUAL REPORT (FINANCIAL YEAR 1922) PRESENTED BY M. J. TIMMERMANS TO THE CHEMICAL SOCIETY OF BELGIUM.*

FOLLOWING the conference of the International Union of Pure and Applied Chemistry at Lyons, held on the 1st June, 1922 (*cf.* ANALYST, 1923, 22), the activities of the Bureau have increased, and the following seven temperature standards are now ready for distribution at a uniform price of 25 francs a sample, with freezing points as follows:—Carbon tetrachloride, −22·9° C.; chlorbenzene, −45·2° C.; chloroform, −63·5° C.; ethyl acetate, −83·6° C.; carbon disulphide, −111·6° C.; ether (stable form), −116·3° C., (unstable form), −123·3° C.; and methylcyclohexane, −126·3° C. These standards reproduce to approximately one-tenth of a degree the scale of low temperatures of the helium thermometer used in the cryogenic laboratory at Leiden. Other standards are in course of preparation.

Following the report of the Commission charged with the choice of a thermochemical standard the International Union has adopted benzoic acid prepared by the Washington Bureau of Standards. This substance is supplied by the Physico-Chemical Bureau in the original flasks in quantities of 30 grms., for two dollars. In response to a previously-expressed wish the American National Aniline and Chemical Company have made the Bureau a gift of 5 kilos each of the following substances: Bromnaphthalene, benzidine, dimethylaniline, diethylaniline, *o*- and *p*-nitrotoluene, and *o*- and *p*-toluidine. These have been prepared with particular care in the course of fractionating large quantities of the industrial products, and will be of great use to the Bureau as starting points in the preparation of standards.

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* *Bull. Soc. Chim. Belg.*, 1923, 2, 95.

These results have been made possible by the grant of 9000 francs from the International Union, but the foreign colleagues, estimating that the grant that the Union could make would not be enough, have decided to appeal for an equal amount from the representatives of Belgian industry, and to show the international interest which attaches to the work of the Bureau. Mr. E. Mond, of Great Britain, is undertaking the necessary organisation.

D. G. H.

The Institute of Chemistry of Great Britain and Ireland.

PASS LIST.

April Examinations, 1923.

The following Associate has passed the examination for the Fellowship:—
In Branch G, Chemical Engineering: A. T. Grisenthwaite, A.C.G.F.C., B.Sc. (Lond.).

The following candidates have passed the examination for the Associateship:—
In General Chemistry: P. J. Brady, H. J. Grayson, L. W. Gregory, G. Loasby, B.Sc. (B'ham), L. W. Marrison, H. W. V. Player, D. A. Smith, and G. J. C. Vineall, B.Sc. (Lond.).

(*Seven candidates failed to satisfy the examiners.*)

By order of the Council,
Richard B. Pilcher, *Registrar and Secretary*.

30, Russell Square, London, W.C.1.,
27th April, 1923.

CAUTION TO INVENTORS.

The following letter has been received from the Registrar and Secretary:

Dear Sir,—In case the matter may not have been brought to your notice already, it has been suggested to me that I should draw your attention to "Caution to Inventors," which has been inserted by the Comptroller-General of Patents in the *Illustrated Official Journal* at the request of the Chartered Institute of Patent Agents:

> "Inventors are advised to beware of suggestions such as are now being issued from a German source to the effect that, for reasons obscurely stated by the German writer, the British inventor should co-operate with him, and in particular should send him by registered letter a sum of money. The communication is fraudulent, and on no account should money be sent."

Yours faithfully,
Richard B. Pilcher, *Registrar and Secretary*.

APPOINTMENT OF PUBLIC ANALYST FOR THE COUNTY AND CITY OF GLOUCESTER.

The Council of the Institute of Chemistry of Great Britain and Ireland advise any Fellow or Associate of the Institute who may contemplate accepting appointment as Public Analyst for the County of Gloucester or for the City of Gloucester on the terms recently advertised to communicate at once with the Registrar.

FILTER PAPER.

The Council of the Institute of Chemistry have appointed a Sub-Committee to consider the production and supply of filter paper in this country.

Chemists who wish to offer criticism or to lay complaints before the Sub-Committee are requested to communicate with the Registrar.

Ministry of Health.

CONDENSED MILK. Circular 393.

The following Circulars have been issued to Authorities (England and Wales) administering the Food and Drugs Acts :—

Sir,

I am directed by the Minister of Health to forward for the information of the Local Authority the enclosed copy of the Public Health (Condensed Milk) Regulations, 1923, prescribing the labelling and composition of condensed milk. The Regulations will come into operation on the 1st October next.

The provisions as to labelling and composition are set out in the Schedules to the Regulations and provision is made for the enforcement of Part II. of the Regulations, which relates to the sale of condensed milk in this country, by the Local Authorities appointing analysts under the Sale of Food and Drugs Acts, on lines following as nearly as may be the procedure under those Acts. Part III. of the Regulations, which relates to the import of condensed milk into this country, will be enforced by the officers of Customs and Excise.

It will be observed that in the enforcement of the Regulations three kinds of offences may need to be dealt with, as mentioned in the following paragraphs:—

(i) There may be an obvious failure to comply with some provision in the First Schedule to the Regulations in regard to labelling (*e.g.* the use of lettering of insufficient size). A chemical analysis of the milk is not required for the purpose of proving an offence of this nature, and it will therefore not be necessary for the purpose of this provision to submit a sample to the Public Analyst.

(ii) The condensed milk may fail to comply with the appropriate standard of composition laid down in the Second Schedule to the Regulations. The sale of such condensed milk would be akin to an offence under Section 6 of the Sale of Food and Drugs Act, 1875, namely, the sale of an article which is not of the nature, substance and quality of the article demanded, and similar procedure is provided for the enforcement of the requirements of the Regulations in regard to composition, including the division of the sample into three parts.

(iii) The label may contain an inaccurate statement of the equivalent quantity of milk or skimmed milk contained in the tin. It is obvious that the division of a sample into three parts would render it impossible to check such a statement, and provision is accordingly made in Article 5 (2) of the Regulations whereby, when a sample is taken for this purpose, the whole tin may be sent unopened to the analyst. It should, however, be observed that, when this is done, the analysis of the sample could not be used for the purpose of proceedings for a breach of Article 4 (2) of the Regulations, should the analysis show a deficiency in milk fat or total milk solids.

The Regulations and this circular are being placed on sale, and copies may be obtained through any bookseller or directly from H.M. Stationery Office, price 1d. net.

I am, sir, your obedient servant,

A. K. MACLACHLAN,

May 4, 1923. *Assistant Secretary.*

STATUTORY RULES AND ORDERS, 1923, No. 509.

PUBLIC HEALTH, ENGLAND.

The Public Health (Condensed Milk) Regulations, **1923,** *dated May* **1, 1923,** *made by the Minister of Health.*

68242.

The Minister of Health in the exercise of the powers conferred upon him by the Public Health Act, 1875, **(a)** the Public Health (London) Act, 1891, **(b)** the Public Health Act, 1896, **(c)** the Public Health (Regulations as to Food) Act, 1907, **(d)** and by Section 8 of the Milk and Dairies (Amendment) Act, 1922, **(e)** and of every other power enabling him in that behalf, hereby makes the following Regulations, with the consent of the Commissioners of Customs and Excise, so far as they apply to the Officers of Customs and Excise, that is to say:—

PART I.

1. These Regulations may be cited as the Public Health (Condensed Milk) Regulations, 1923, and shall come into operation on the 1st day of October, 1923.

2. (1) In these Regulations unless the context otherwise requires—

"The Minister" means the Minister of Health;

"Local Authority" means any Local Authority authorised to appoint an analyst for the purposes of the Sale of Food and Drugs Acts, 1875 to 1907, and "public analyst" means an analyst so appointed;

"Officers of Customs and Excise" includes any person acting under the authority of the Commissioners of His Majesty's Customs and Excise;

"Condensed Milk" means milk or skimmed milk which has been concentrated by the removal of part of its water, whether with or without the addition of sugar, and includes the article commonly known as "evaporated milk" but does not include the article commonly known as "dried milk" or "milk powder";

"Skimmed milk" includes separated or machine-skimmed milk;

"Gross weight" of a tin or other receptacle means the weight of the tin or other receptacle and of its contents;

"Importer" includes any person who, whether as owner, consignor or consignee, agent or broker, is in possession of or in anywise entitled to the custody or control of any condensed milk brought from a place situate outside the United Kingdom, the Channel Islands and the Isle of Man; and "import" shall be construed accordingly;

Percentages shall be calculated by weight.

(2) The Interpretation Act, 1889, **(f)** applies to the interpretation of these Regulations as it applies to the interpretation of an Act of Parliament.

PART II.

3. The Local Authority shall enforce and execute this Part of these Regulations, and for this purpose shall make such enquiries and take such other steps as may seem to them to be necessary for securing the due observance of this Part of the Regulations in their district.

4. No person shall sell or expose for sale or deposit in any place for the purposes of sale, or despatch or deliver to any purchaser, broker or agent any condensed milk intended for human consumption unless the condensed milk—

(1) is contained in a tin or other receptacle which is labelled in the manner prescribed in the First Schedule to these Regulations; and

(2) contains not less than the appropriate percentages of milk fat and milk solids as specified in the Second Schedule to these Regulations:

Provided that—(*a*) The provisions of this Article shall not apply in any case where the condensed milk is intended to be exported or is contained in a tin or other receptacle whose gross weight exceeds five pounds; and (*b*) Where in any public refreshment room, restaurant, shop or other public premises condensed milk is delivered to a purchaser or other person for consumption on the premises, the receptacle containing the condensed milk shall not be required to be labelled in the manner prescribed by these Regulations.

(a) 38–9 V. c. 55. **(b)** 54–5 V. c. 76. **(c)** 59–60 V. c. 20.
(d) 7 E. 7. c. 32. **(e)** 12–3 G. 5. c. 54. **(f)** 52–3 V. c. 63.

5. (1) The Medical Officer of Health, and any person authorised by him or by the Local Authority in writing, may procure any sample of condensed milk, and where an analysis is required for the purposes of these Regulations shall submit the sample to the Public Analyst and shall forthwith notify to the seller or his agent selling the condensed milk his intention to have the same analysed by the Public Analyst.

(2) Except where the sample is procured for the purpose of testing the quantity of milk or skimmed milk of which the contents of a tin or other receptacle are the equivalent, the provisions of Section 14 of the Sale of Food and Drugs Act, 1875, (**a**) as amended by Section 13 of the Sale of Food and Drugs Act, 1899, (**b**) relating to the division of the sample into three parts and the separation, marking and disposal of such parts shall apply.

6. Any Officer authorised by the Minister and any officer of the Local Authority duly authorised by the Authority in writing shall have power to enter at all reasonable times any premises where condensed milk is prepared packed labelled or stored and to inspect any process carried on therein and to take samples of any article used or capable of being used in the preparation of condensed milk and of any labels designed to be used for affixing to tins or other receptacles of condensed milk.

7. Where the Local Authority on a report to them from the Public Analyst or otherwise are of opinion that a consignment of condensed milk deposited within their district and intended for sale for human consumption does not comply with the requirements of these Regulations they shall endeavour to ascertain where it was manufactured and labelled. If it is ascertained that such condensed milk was manufactured or labelled at a place in England or Wales, the Local Authority shall communicate the facts which they have ascertained to the Local Authority for the district in which such place is situated. If it is ascertained that such condensed milk was manufactured or labelled at a place not in England or Wales, the Local Authority shall communicate the facts to the Minister.

PART III.

8.—(1) Subject to any directions given by the Commissioners of Customs and Excise after consultation with the Minister, the Officers of Customs and Excise shall enforce and execute this Part of these Regulations and may take such samples of consignments of imported condensed milk as may be necessary for that purpose.

(2) Where an Officer of Customs and Excise takes a sample for the purpose of analysis he shall send the sample to the Government Chemist and the Government Chemist shall send a portion thereof to the importer.

(3) If in any case the Commissioners of Customs and Excise are of opinion that an offence against this Part of these Regulations has been committed, they shall communicate to the Minister for his information the name of the importer and such other facts as they may possess or may obtain as to the destination of the consignment.

9. No condensed milk intended for sale for human consumption shall be imported into England and Wales unless the same—

(1) is contained in a tin or other receptacle which is labelled in the manner prescribed in the First Schedule to these Regulations; and

(2) contains not less than the appropriate percentages of milk fat and milk solids as specified in the Second Schedule to these Regulations:

Provided that the provisions of this Article shall not apply in any case where the condensed milk is intended to be re-exported or is contained in a tin or other receptacle whose gross weight exceeds five pounds.

PART IV.

10. In any proceedings under these Regulations the certificate of the Government Chemist or the Public Analyst, as the case may be, of the result of the chemical examination of a sample shall be sufficient evidence of the facts therein stated unless the defendant requires that the person who made the examination be called as a witness.

11. A person, in relation to anything within his knowledge, shall truly answer all such questions put to him by the authorities authorised to enforce and execute these Regulations or their officers or by an officer authorised by the Minister as may be necessary for the purposes of these Regulations, and shall produce for inspection all such books as the authority or officer may reasonably require for the purposes of ascertaining the persons or places from which condensed milk has been obtained and to whom and where it has been consigned or otherwise.

(**a**) 38-9 V. c. 63. (**b**) 62-3 V. c. 51.

12. In any proceedings under these Regulations, where the fact that any condensed milk has been dealt with contrary to these Regulations has been proved, if the defendant shall desire to rely upon any exception or provision contained in these Regulations with reference to condensed milk intended for export or re-export, it shall be incumbent upon him to prove that the condensed milk was so intended.

The First Schedule.

RULES WITH RESPECT TO THE LABELLING OF CONDENSED MILK.

1. Every tin or other receptacle containing condensed milk shall bear a label upon which is printed such one of the following declarations as may be applicable or such other declaration substantially to the like effect as may be allowed by the Minister:—

(i) In the case of full cream milk (unsweetened):—

> CONDENSED FULL CREAM MILK,
> UNSWEETENED.
>
> THIS TIN CONTAINS THE EQUIVALENT OF
> (*a*) PINTS OF MILK.

(ii) In the case of full cream milk (sweetened):—

> CONDENSED FULL CREAM MILK,
> SWEETENED.
>
> THIS TIN CONTAINS THE EQUIVALENT OF
> (*a*) PINTS OF MILK, WITH SUGAR ADDED.

(iii) In the case of skimmed milk (unsweetened):—

> CONDENSED MACHINE-SKIMMED
> MILK [OR CONDENSED SKIMMED
> MILK], UNSWEETENED.
>
> UNFIT FOR BABIES.
>
> THIS TIN CONTAINS THE EQUIVALENT OF
> (*a*) PINTS OF SKIMMED MILK.

(iv) In the case of skimmed milk (sweetened):—

> CONDENSED MACHINE-SKIMMED
> MILK [OR CONDENSED SKIMMED
> MILK], SWEETENED.
>
> UNFIT FOR BABIES.
>
> THIS TIN CONTAINS THE EQUIVALENT OF
> (*a*) PINTS OF SKIMMED MILK, WITH SUGAR ADDED.

2. The declaration shall in each case be completed by inserting at (*a*) the appropriate number in words and figures, *e.g.* "one and a half (1½)," any fraction being expressed as eighths, quarters or a half.

For the purposes of these Rules milk means milk which contains not less than 12·4 per cent. of milk solids (including not less than 3·6 per cent. of milk fat) and skimmed milk means milk which contains not less than 9 per cent. of milk solids other than milk fat.

3. The prescribed declaration shall be printed in dark block type upon a light coloured ground within a surrounding line and no other matter shall be printed within such surrounding line. The type to be used for the last sentence of the declarations set out above shall be not less than one-eighth of an inch in height (or if the gross weight of the tin or other receptacle does not exceed twelve ounces, one-sixteenth of an inch in height), and that to be used for the remainder of the said declarations shall be not less than one-quarter of an inch in height (or if the gross weight of the tin or other receptacle does not exceed twelve ounces, one-eighth of an inch in height).

4. The label shall in addition bear the name and address of the manufacturer of the condensed milk or of the dealer or merchant in the United Kingdom for whom it is manufactured.*

5. The label shall be securely affixed to the tin or other receptacle so as to be clearly visible. If there is attached to the tin or other receptacle a label bearing the name, trade mark, or design representing the brand of the condensed milk, the prescribed declaration shall be printed as part of such label.

6. There shall not be placed on any tin or other receptacle containing condensed milk—

(*a*) any comment on, explanation of, or reference to either the statement of equivalence contained in the prescribed declaration or the words "machine skimmed," "skimmed," or "unfit for babies"; or

(*b*) any instructions as to dilution, unless either—

(i) the fluid produced in accordance with such instructions would contain not less milk fat and not less milk solids than milk or skimmed milk as defined in Rule 2 of this Schedule as the case may require; or

(ii) such instructions clearly specify that the fluid so produced is not of equivalent composition to milk or skimmed milk as the case may be.

7. Wherever the word "Milk" appears on the label of a tin or other receptacle of condensed skimmed milk as the description or part of the description of the contents, it shall be immediately preceded or followed by the word "Machine-Skimmed" or "Skimmed" as the case may require.

The Second Schedule.

All condensed milk shall contain not less than the appropriate percentages of milk fat and milk solids as specified in the following Table:—

Description of Condensed Milk.	Percentage of milk fat.	Percentage of all milk solids, including fat.
1. Full cream, unsweetened	9·0	31·0
2. Full cream, sweetened	9·0	31·0
3. Skimmed, unsweetened	—	20·0
4. Skimmed, sweetened	—	26·0

Given under the Official Seal of the Minister of Health this First day of May in the year One thousand nine hundred and twenty-three.

A. K. MACLACHLAN, *Assistant Secretary, Ministry of Health.*

The Commissioners of Customs and Excise hereby consent to the foregoing Regulations so far as they apply to the Officers of Customs and Excise.

A. J. DYKE, W. YOUNG, *Two of the Commissioners of His Majesty's Customs and Excise.*

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* In the case of imported condensed milk, the provisions of section 16 of the Merchandise Marks Act, 1887 (50–1 V. c. 28), must also be complied with if the label bears the name or trade mark of a dealer or merchant in the United Kingdom.

Note.—The Public Health Act, 1896, provides by sub-section (3) of Section 1 that if any person wilfully neglects or refuses to obey or carry out, or obstructs the execution of any regulations made under any of the enactments mentioned in that Act he shall be liable to a penalty not exceeding £100, and, in the case of a continuing offence to a further penalty not exceeding £50 for every day during which the offence continues.

The power of making regulations under the Public Health Act, 1896, and the enactments mentioned in that Act, is enlarged by the Public Health (Regulations as to Food) Act, 1907, as amended by the Milk and Dairies (Amendment) Act, 1922.

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SALE OF MILK DEFICIENT IN FAT.

Circular 399 (England and Wales).

May 16, 1923.

SIR,

I am directed by the Minister of Health to state that he has had under consideration Circular 325 of the 17th of July, 1922, with reference to prosecutions for selling milk deficient in fat.

From information which he has had before him it is evident that this Circular has been widely misunderstood and to some extent misrepresented, with the result that it has not produced the effect which was intended.

In the circumstances he has decided to withdraw the Circular, feeling that he can rely on the responsible local authorities to administer the Sale of Food and Drugs Acts with due fairness and consideration to the various interests concerned.

I am, sir, your obedient servant,

A. K. MACLACHLAN,

Assistant Secretary.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Estimation of Starch in Presence of Interfering Polysaccharides. G. P. Walton and M. R. Coe. (*J. Assoc. Off. Agric. Chem.*, 1923, **6**, 350–354.)—The following method has been worked out to facilitate the estimation of sugars and starch in the presence of mucilaginous and pectinous materials, such as linseed cake and apple pomace. The substance under examination is ground to pass a 60-mesh sieve, and from 2 to 6 grms. are weighed out, transferred to a filter and extracted with 5 portions of ether. The residue is extracted with 300 c.c. of alcohol of 35 per cent. strength by volume for linseed meal, or 25 per cent. for apple pomace, and later with several portions of 95 per cent. alcohol, followed by ether. After standing overnight, to allow the remaining alcohol and ether to evaporate, the residue is mixed with 20 or 30 c.c. of water to a smooth paste, diluted to about 150 c.c., heated on a boiling water bath, and finally boiled briskly. After cooling to 50° C., 20 c.c. of 5 per cent. cold malt extract are added, the temperature being gradually raised to 70° C. and maintained at this point for 30 minutes, after which it is increased to 80° C. for 10 minutes, and the mixture is then heated to 100° C. The conversion is completed by cooling the mixture to 55° C., adding a further

20 c.c. portion of malt extract, and maintaining the temperature at 55° C., with occasional shaking, for 1 hour. To the liquid 316 c.c. of 95 per cent. alcohol are added in small portions, with thorough shaking, and, after cooling to 15° C., the liquid is diluted to 500 c.c., plus 3 c.c. for each 4 grms. of solid matter present, and is thoroughly mixed by pouring from one beaker into another, after which it is filtered. Two hundred c.c. of the filtrate are evaporated on a water-bath to 15 or 20 c.c., diluted to 200 c.c. with hot water and, after the addition of 20 c.c. of 25 per cent. hydrochloric acid, heated in a boiling water bath under a reflux condenser for 2½ hours. The liquid is cooled, 1 c.c. of 10 per cent. phosphotungstic acid in 1 per cent. hydrochloric acid solution added, and, after standing for 15 minutes, the liquid is diluted to 250 c.c. and filtered. To 200 c.c. of the filtrate 10 c.c. of 44 per cent. sodium hydroxide solution are added, and neutralisation is almost completed by adding anhydrous sodium carbonate, after which the liquid is cooled, diluted to 250 c.c. and filtered, if necessary. The dextrose present is estimated gravimetrically in 50 c.c. of the filtrate by Munson and Walker's or Allihn's method, the result being corrected for the dextrose derived from the malt extract present by a similar estimation carried out with the extract alone. The method yields results showing a maximum error of −2·8 per cent., with an average of −1·3 per cent. on the weight of starch present. Since particular care is essential for obtaining reliable results, full details of procedure are given in the original paper. T. J. W.

Electrometric Titration of Reducing Sugars. W. L. Daggett, A. W. Campbell and J. L. Whitman. (*J. Amer. Chem. Soc.*, 1923, **45**, 1043–1045.)—The following method of titrating reducing sugars electrometrically with Fehling solution gives a more satisfactory end-point if the alkaline tartrate solution contains only 50 grms. of sodium hydroxide per litre, both solutions being otherwise as described by Leach (*Food Inspection and Analysis*, 1905, 486). Ten c.c. of each of the component solutions of Fehling solution are mixed and diluted with 50 c.c. of water, the liquid being heated to boiling and the sugar solution added rapidly until the end-point is reached. When the first additions of sugar solution are made, the deflections of the galvanometer in circuit with the titration vessel are small and somewhat irregular, and may be kept very nearly at zero by slight changes of the adjustable resistance. At the end-point one drop of the sugar solution produces a large deflection, and a considerable alteration in the resistance is necessary to bring it again to zero. When the conditions are uniformly observed the results obtained are comparable, except in so far as they are affected by daily changes in the barometric pressure (*cf.* Quisumbing and Thomas, ANALYST, 1922, **47**, 27). The method has not yet been applied to the estimation of very small amounts of reducing sugars, or to solutions containing large proportions of other sugars, such as sucrose. T. H. P.

Action of Alkaline Earths upon the Estimation of Sugars by Fehling Solution. L. Eynon and J. H. Lane. (*J. Soc. Chem. Ind.*, 1923, **42**, 143–146T.)—Experiments are described which show that the presence of calcium, barium or strontium salts, even in concentrations as low as 0·002 *N*, in a sugar solution introduces considerable errors in both the volumetric and gravimetric Fehling estimations, low results being obtained. This effect is shown with dextrose, lævulose, maltose and lactose, but is more pronounced with the last-named, in which the presence of 0·01 *N* calcium chloride caused an error of −6·6 per cent. on the total sugar present. This result is not obtained with solutions of magnesium, aluminium or potassium salts, although the use of tap water containing calcium in preparing solutions introduces considerable error. By the use of sodium or potassium oxalate as a precipitant these errors may be avoided, but sodium carbonate and phosphate are not entirely effective. In the examination of commercial sugars both the lead acetate used for clarifying and any calcium salts present may be removed by the addition of sodium oxalate and a little alumina cream to assist filtration. The accuracy of the titration is unaffected by any excess of oxalate remaining in solution. The contradictory results obtained by Meade and Harris (ANALYST, 1916, **41**, 247) are discussed and explained according to the above results. T. J. W.

Adulteration of Ergot. G. Tanret. (*Ann. Falsificat.*, 1923, **172–173**, 73.)—As a result of the exceedingly high price of this drug, a false ergotinine "crystallised and pure" has been put on the market. It is a yellow amorphous powder, without definite characteristics. In addition to this, a spurious ergot of rye is being sold in Paris under the name of Spanish or Portuguese Ergot. Close examination shows this to consist of a mixture of two kinds of grains, the one being greyish and more or less furrowed (genuine ergot), whilst the other is blacker and has the following characteristics:—The grains have about the same dimensions as true ergot (10 to 25 mm. by 2 to 4 mm.), but grains larger or smaller are exceptional. They are more or less curved and less tapering than the genuine drug, their ends being often rounded. When thrown into water they sink (spec. grav. 1·264), whilst true ergot (spec. grav. 0·984) floats. On fracture they appear yellowish grey up to the edge, whereas ergot is most often white with a pinkish circumference. If ground with the teeth one notices a mealy taste without the sweet-bitter after-taste of true ergot. A more accentuated difference is shown by their behaviour in weak alcohol or water. Genuine ergot scarcely colours these liquids after several minutes, and imparts only a slight yellow or very pale pink tint; the spurious grains, however, immediately colour dilute alcohol or water an intense violet-black, and, on gentle friction, the grains are left white with small rose-coloured patches, which can be separated by more vigorous friction. The violet solution was found to be a common ink of iron and tannin. The white grains showed the characteristics of wheat starch tinted with red ink, and gave none of the alkaloidal reactions of ergot. The adulteration amounted to 15 to 18 per cent. R. F. I.

Chemical Examination of Organo-therapeutic Powders. R. Fabre and H. Penau. (*J. Pharm. Chim.*, 1923, **27**, 281–290.)—The powders dealt with included preparations from the pancreas, pituitary body, thyroid, liver and corpora lutea, and the object of the examination was to detect adulteration by such substances as lactose, sucrose, starch, talc, chalk, etc., and the presence of preservatives such as, for example, salt, boric acid, sodium fluoride, and formaldehyde, which are often present in considerable proportions. Moisture (estimated by drying the product for 6 hours at 105° C.) and ash (soluble and insoluble) should always be estimated. It was found that, speaking generally, if the soluble ash exceeded 6 per cent., an addition of sodium fluoride, boric acid or chlorides was to be suspected. Should the insoluble ash be over 5 per cent., chalk, talc or silica should be looked for, and the presence of chalk is still more probable if at the same time the alkalinity is above normal; the presence of talc and silica may be confirmed by ordinary analytical methods. Salting of the organs before preparation is to be suspected when the total chlorides exceed 4 per cent., and the quantity of salt found may be as much as 10 or 15 per cent. of the weight of the extract. The authors have obtained the following average figures for the ratio of soluble to (insoluble) ash:—Ovarine, 53; hepatine, 45; thyroid, 53; and pituitary body, 32. Pituitary body powders were found to have a rather higher insoluble ash than other preparations owing to the presence of bone splinters, very difficult to eliminate from the fresh organ. If, however, the proportion of insoluble ash exceeds a determined limit it is justifiable to assume that there is adulteration from added mineral matter, or that the organs have been insufficiently cleaned. The following table gives some of the authors' results for pure products in grms. per 100 grms. of product.

	NaCl	Ash Soluble (C.S.)	Ash Insoluble	Total Ash (C.T.)	$\frac{\text{C.S.}}{\text{C.T.}}$ Per Cent.	Alkalinity as Na_2CO_3
Hepatine A. ...	0·06	1·90	3·20	5·10	40	1·02
Hepatine B. ...	0·05	2·23	0·91	4·14	52	1·45
Pituitary body ...	0·35	2·16	4·59	6·75	32	2·56
Pituitary body (not cleaned)...	—	—	—	20·85	—	4·24
Thyroid ...	2·01	4·01	3·48	7·49	53	2·02
Ovarine A. ...	1·99	4·18	4·31	8·49	49	2·60
Ovarine B. ...	2·92	—	1·96	—	—	—
Ovarine pure, C. ...	1·39	4·35	4·19	8·54	51	2·16
Ovarine pure, D. ...	1·96	4·17	2·68	6·85	61	0·90
Ovarine pure, E. ...	1·65	4·90	3·50	8·40	58	1·31
Ovarine pure, F. ...	2·50	—	1·40	—	—	—

Various adulterated samples of ovarine gave the following percentages for salt and insoluble ash respectively:—Ovarine I., 2·4 and 52·26; ovarine II., 13·6 and 8·3; ovarine III., 24·57 and 1·3; ovarine IV., 14·62 and 0·875; ovarine V., 6·786 and 2·46; ovarine VI.,5·428 and 1·96. In addition, ovarine VI. had a total ash of 12·46 per cent., and showed the presence of fluoride and boron, and ovarine VII. contained 63 per cent. of lactose. Samples II. to V. inclusive were salted, and the first sample showed the addition of silica. D. G. H.

The Codex Reaction for Ethyl Chloride. A. Richaud. (*J. Pharm. Chim.*, 1923, **27**, 329–332.)—The French Codex states that "ethyl chloride should not immediately precipitate silver nitrate in aqueous solution or in cold alcohol," and this statement is capable of two interpretations. (1) Ethyl chloride, either alone or with the addition of cold alcohol, should give no precipitate on adding an aqueous solution of silver nitrate. (2) Ethyl chloride should give no precipitate, either on addition of silver nitrate in aqueous solution or on adding an alcoholic solution of silver nitrate. Studying the reaction from the first point of view, the conclusion is arrived at that the cloudiness is insignificant when the silver nitrate is added to ethyl chloride previously mixed with a little alcohol, and, if enough alcohol is used, no cloudiness results provided the ethyl chloride is pure. In the second case, a precipitate is always first formed on the addition of an alcoholic solution of silver nitrate to ethyl chloride (due to the fact that silver nitrate is not soluble in ethyl chloride), but in the case of pure ethyl chloride it always disappears on the addition of excess of the reagent, or of water, or of alcohol. In order to avoid this confusion other Pharmacopæias specify that the reaction should be carried out, not directly on the ethyl chloride, but either on the liquid obtained by bubbling the vapour through water, or after the addition of a definite quantity of alcohol, and it is suggested that such a modification should be introduced into the French Codex. D. G. H.

Biochemical, Bacteriological, etc.

Modified Technique in Estimation of Vitamin *B* by Use of Rats. H. Steenbock, M. T. Sell and E. M. Nelson. (*J. Biol. Chem.*, 1923, **55**, 399–410.)—Observations made during experiments conducted to determine the influence of excretal mineral salts upon the growth of rats showed that those animals without access to their fæces, owing to the use of a cage fitted with a perforated false bottom, developed typical symptoms of vitamin *B* deficiency, whilst others from which the fæces were not separated and which developed coprophagistic tendencies, remained entirely free from such symptoms. Further, on allowing the rats which exhibited retarded growth and polyneuritis access to their fæces by removing the false bottoms of the cages, these animals rapidly recovered their health. These effects were shown to be independent of the salts present, and are apparently due to the presence of vitamin *B* in the excreta. When rats are prevented, as far as possible, from ingesting their fæces at least 60 per cent. of the ration provided must consist of cereals in order to maintain maximum growth. The authors indicate that owing to the absence of knowledge concerning this factor many of the results previously obtained in research on vitamin *B* are valueless.

T. J. W.

Estimation of the Number of Bacteria in Soil. C. L. Whittles. (*J. Agric. Sci.*, 1923, **13**, 18–48.)—Examination of the usual shaking methods for the enumeration of the bacteria in soil shows that the results obtained are quite worthless, being much too low. The motion imparted by hand or mechanical shaking is not of the type required for the dispersion of the soil particles, and the prolongation of the time of shaking has but little effect; the addition of beads is also of no value, as it only reduces the number of colonies. Sodium carbonate (0·05 per cent. in the dilution liquid) causes a marked increase in the number of colonies. Direct examination of smears and counts of films give results higher and nearer the truth. Films are prepared from 10 per cent. suspensions in water, 0·01 c.c. of which is spread over an area of 4 sq. cm., dried, and then fixed by means of a dilute solution of collodion in alcohol-ether, and the organisms in several known areas are counted under a 1/12th in. oil immersion objective. The method is difficult, however, and there are very large experimental errors. The best results are obtained by a vibration method as follows: The dilution liquid consists of 0·2 per cent. sodium chloride, 0·05 per cent. sodium carbonate, and a little gelatin dissolved in water. Twenty-five grms. of the soil are shaken with 250 c.c. of the medium, 2 c.c. are then pipetted into the vibrator vessel, and diluted to 2 litres; 2 c.c. of this dilution are twice similarly diluted by means of the vibrator, giving a final dilution of 1:10, from which agar plates are prepared and incubated at 22° C. The vibrator consists of a cylindrical glass tube of capacity 100 c.c., with a celluloid bottom which is tapped by an electric bell hammer; into this vessel the dilution medium is siphoned to the bottom, and the suspension is drawn off from the surface of the liquid and run into a bottle marked at 2 litres. The whole apparatus is sterilised before use, and between the dilutions. Plates are counted daily, but there is no advantage in continuing the counts for more than four days, as the organisms have been liberated from their gel coatings, and grow more rapidly than under the ordinary shaking conditions. The degree of dispersion of a soil in relation to its moisture-holding properties has also been examined by means of the vibrator. A complete bibliography on the bacterial content of soil is appended. H. E. C.

Method for Separate Extraction of Vacuole Contents and Protoplasmic Material from Leaf Cells. A. C. Chibnall. (*J. Biol. Chem.*, 1923, **55**, 333–342.) —It has been observed by the author that immersion of fresh plant leaves in ether, caprylic alcohol or chloroform causes extreme flaccidity and irreversible plasmolysis of the cells in a few seconds. Upon this observation the following method is based:—The leaves are immersed in ether for 1 minute, and the mass is wrapped in a filter cloth and pressed between iron plates in a Buchner press, a clear brownish liquid containing a small quantity of protein and large amount of ash being thus obtained. The remainder of the vacuole contents are removed by allowing the press cake to absorb 0·002 *N* hydrochloric acid, and subsequently squeezing it again, this procedure being repeated several times. The protoplasmic contents of the cells are removed from the residue by grinding the mass with water in a mill, when a portion of the protoplasmic protein passes into solution. The leaf cells are not ruptured by the extraction and pressure required for removal of the vacuole contents, and the amount of nitrogen present in the solids contained in the first exudate and the succeeding extracts is constant. T. J. W.

Refractometric Estimation of Serum Proteins. B. S. Neuhausen and D. M. Rioch. (*J. Biol. Chem.*, 1923, **55**, 353–356.)—The authors point out that the factor of 0·00172 given by Reiss (*Z. Elektrochem.*, 1908, **14**, 613) is too low, since the increase of refractive index produced by 1 per cent. of albumin is 0·00183, and of globulin 0·00227. In order to determine the most correct factor human blood serum was "ultra-filtered" through collodion tubes, and the R.I. of the filtrate was determined. The difference between this result (minus that of distilled water) and that obtained with the serum itself was used to determine the R.I. increment of the proteins. The serum was mixed with an equal volume of saturated ammonium sulphate solution and, after filtration, the R.I. obtained was a combination of that due to half-saturated ammonium sulphate solution, the non-protein constituents and one-half of the albumins originally present. The value yielded by the albumins, divided by 0·00183, was assumed to give the percentage of these bodies present; the value for the globulins was then calculated, and their percentage deduced by using the factor 0·00227. The total percentage of proteins present was then calculated and compared with results obtained by Kjeldahl estimations. Fair agreement was shown between the two sets of results, the maximum error being +8·1 per cent. of the protein present, whereas similar results calculated from the factor given by Reiss showed an error of +17·5 per cent. It is suggested that the mean factor of 0·00194 will yield the most correct values with human serum.
T. J. W.

Error due to Photochemical Action in the Folin and Wu Estimation of Uric Acid. H. Rogers. (*J. Biol. Chem.*, 1923, **55**, 325–331.)—Estimations made of uric acid in solutions of known concentration and in beef blood and human blood by the above method (*J. Biol. Chem.*, 1919, **38**, 8 and 450), and the modification described by Folin (Analyst, 1923, 79), have shown that exposure to actinic light leads to a loss of uric acid, varying from 16 to 92 per cent. This loss is approximately proportional to the intensity of and time of exposure to light, but diminishes as the proportion of uric acid present is reduced. The effect of light is greatest during the period when the uric acid is present in the silver precipitate. The action of light is increased by the addition of a larger proportion of lactic acid to the silver lactate-lactic acid precipitating reagent. These errors may be obviated by carrying out the estimation in non-actinic light, or by shielding the centrifuge tubes by trunnion-cups and tinfoil until the uric acid has been decanted from them. The results obtained in this investigation are tabulated in detail.
T. J. W.

Toxicological and Forensic.

Dermatitis from Dyed Fur. H. C. Semon. (*Brit. Med. J.*, 1923 (Mar. 17), 467; (Apr. 7), 613.)—Attention is directed to a current epidemic of "fur dermatitis" among out-patients of the hospitals. The eruptions have all been of the same type, consisting of a blotchy erythema, limited in the earlier cases to the lateral aspects of the neck and face, whilst the later cases have shown infiltration with a endency to vesiculation and "weeping." In every case direct association by contact of the fur collar with the neck and chin could be demonstrated, and further support of the diagnosis was obtained in two cases by applying a scrap of the fur under strapping plaster (and against a control) to the anterior aspect of the thigh. Erythema occurred in both subjects of the experiment where the fur was applied, and within 24 hours of the application. The coats responsible all had fur collars of a dark flat variety, of very poor quality, and known to the trade as "dyed coney."

An analysis has been made by H. Skinner of fur held responsible for one of the cases. The fur yielded nothing to cold water, but when digested with dilute solutions of salt, alkalis or acids or with wool fat (for some hours) gave extracts of a colouring matter which gave reactions consistent with those of metaphenylenediamine base. In this case a dichromate mordant appeared to have been used, and the fact that the dyestuff could be extracted pointed to its insufficient fixation at this stage. It is well known that the meta-base is considered more poisonous to the skin than its isomer, paraphenylenediamine. It is significant to note that the dye which has been isolated is soluble in saline liquids and in wool fat, which have their analogues in the sweat and sebaceous secretions of the skin.

Dermatitis from Dyed Fur. A. C. Roxburgh. (*Brit. Med. J.*, 1923, (Mar. 24), 534–535.)—An account is given of observations made in connection with this subject in the skin department of St. Bartholomew's hospital during the last 3 months. It is pointed out that many thousands of women are wearing "beaver coney" collars without any ill result, and that even the large number of patients with dermatitis due to this fur must form a very small percentage of the total wearers. Although the outbreak is more widespread than usual, it is not a new phenomenon, and analogous cases have been recorded, *e.g.* in 1913 by Blaschko (*Deut. Med. Woch.*, 1913, No. 49), in 1916 in America by Olson (*J. Amer. Med. Assoc.*, Mar. 18, 1916), and in 1922 by Rasch (*Ugekrift for Laeger*, Apr. 13, 1922). Since Jan. 1922 there have been 33 cases at St. Bartholomew's Hospital of women and girls, from 15 to 50 years of age, suffering from dermatitis due to wearing "beaver coney" collars. This fur is rabbit's skin dyed brown. The length of time for which different patients have worn their furs before the appearance of the rash has varied from 2 to 20 weeks. Two explanations have been suggested to account for the latent period. Olson (*loc. cit.*) considers that it is only when the fur gets damp from rain or perspiration that the dye is absorbed by the skin, and the patient develops the rash for the first time. In the author's opinion, however, a more probable explanation is that the delay is due to the patient gradually developing a sensitiveness to the irritant in question. In one case cited a patient had developed a rash on the neck after wearing the fur for 11 weeks. She was directed to remove the fur collar from her coat and to carry it over her arm for a few minutes, and within 24 hours developed on her wrist, where the fur had rested, the typical erythema. In most of the previously recorded cases, the dye incriminated has been paraphenylenediamine, often known in the trade as "ursol," which is also the active constituent of a popular hair dye well known to produce severe dermatitis in sensitive persons. In the oxidation of paraphenylenediamine an exceedingly irritating substance, quinone dichlordi-imine, is formed, and it is possible that this substance has been left in the furs in question, owing to insufficent oxidation and to incomplete removal of the excess of dye in the finishing process.

Dyed Furs. W. F. Castle. (*Brit. Med. J.*, 1923, (Mar. 24), 535.)—The type of fur which seems to be chiefly to blame for the dermatitis which is now frequently met with in the out-patient departments, is "beaver dyed coney," *i.e.* rabbit skins dyed in imitation of more expensive skins. The furs seem to be innocuous unless the wearer has a greasy skin, when the colouring matter appears to dissolve in the fatty acids. The chief dyes used are the following:—*Light brown*, pyrogallol; *medium brown*, metatoluylene diamine base; *dark brown*, metaphenylene diamine base; *red-brown*, para-amino-phenol hydrochloride; *deep black*, paraphenylenediamine; *blue-black*, nigrosine and nigrosine with paraphenylenediamine. The cheap furs are apparently not finished, *i.e.* the mordants used are not neutralised. Before dyeing, the hairs are degreased, and in some cases subjected to preliminary treatment with bleaching powder to increase their affinity for the dye. The organic amines, which are the principal dyestuffs used, are sold under the name of "ursols," "furols," "fantols," etc. They are usually applied to unmordanted skins for light shades, and to mordanted skins for medium and dark shades. The most usual mordants are potassium dichromate and the sulphates of iron and copper, which are used in baths of weak acids, such as acetic or tartaric acid. In the author's opinion it is doubtful whether it is an unneutralised mordant or the dye itself which causes the dermatitis.

Toxicity of Cadmium. (*Chem. Trade J.*, 1923, **72**, 518.)—In connection with the recent death of a London workman following the inhalation of cadmium fumes, it is of interest to note some of the latest results obtained by the U.S. Bureau of Chemistry on the toxicity of cadmium. With a concentration of cadmium greater than 125 parts per million in the diet of normal rats, death occurred in every male in about fifty days. Some of the females survived a very much longer time. A concentration of cadmium of 62·5 parts per million had no deleterious effect. No evidence of cumulative systematic action was observed with low concentration of the metal.

Hydrolysis of the Xanthylated Derivatives of Veronal and Hypnotics of the Barbituric Series, and its Toxicological Importance. R. Fabre. (*J. Pharm. Chim.*, 1923, **27**, 337–339.)—Veronal and the hypnotic derivatives of barbituric acid form xanthylated derivatives by condensation in acetic acid (ANALYST, 1922, **47**, 523), and Fosse has shown (*Bull. Soc. Chim.*, (3), **36**, 1006) that these derivatives are hydrolysed by the hydracids. Xanthylmalonic acid, when treated with hot alcohol saturated with hydrogen chloride, yields malonic acid, xanthine and acetaldehyde, and the same reaction takes place with ease in the case of dixanthyl-alkyl-malonyl-ureas. The test is carried out as follows:—One grm. of dixanthylveronal, for example, is heated with 5 c.c. of 20 per cent. alcohol saturated with hydrogen chloride, under a reflux condenser for one hour. The xanthylated product dissolves, giving a dark green solution which, when poured into 25 c.c. of distilled water, becomes decolorised and deposits a copious precipitate. This is partly dissolved by treatment with 0·1 *N* sodium hydroxide solution, any insoluble or amorphous substances formed during hydrolysis being then eliminated by shaking three times with ether. The alkaline liquid is next acidified with dilute sulphuric acid, and the precipitated veronal dissolved by shaking with successive portions of 10 c.c. of ether. The ether is evaporated, and the crystalline residue weighed and its melting point determined. Two actual estimations of veronal from 1 grm. of the xanthylated derivative gave respectively 0·328 and 0·330 grm. of veronal of melting point 190–191° C., the theoretical yield being 0·338 grm. This reaction is very general, and may be applied to such xanthylated derivatives of barbituric acid as phenylethyl urea (gardenal), diallyl urea (dial), butylethyl urea, and isobutylethyl-malonylurea, and the resulting products are readily identified. D. G. H.

Water Analysis.

Estimation of Temporary Hardness in Water. W. R. Atkin and A. Gardner. (*J. Soc. Leather Trades' Chem.*, 1923, **7**, 87–90.)—In estimating the temporary hardness of water by Hehner's method better results are obtained by the use of brom-phenol blue than of methyl orange as indicator. The colour change of brom-phenol blue takes place between $P_H = 2{\cdot}8$ and 4·6, and the end-points are remarkably sharp. It must be borne in mind, however, that the presence of the salts of weak acids, such as peaty acid, would vitiate this sharpness, owing to the liberation of the weak acids by the hydrochloric acid used in the titration, and the consequent formation of buffer mixtures with the undecomposed salts. In such a case a comparatively large amount of hydrochloric acid would only produce a small alteration in the P_H value.

Rapid Estimation of Iodine in Mineral Waters containing Sulphides. M. J. Dubief. (*Ann. Falsificat.*, 1923, **172–173**, 80.)—If a water containing sulphides, sulphites and organic matter is treated with potassium permanganate, first in alkaline and then in acid solution, immediate oxidation takes place. Chlorine, bromine and iodine are liberated, and the iodine can be estimated as follows:—Fifty or 100 c.c. of the water, according to the iodine content, are poured into a 100 c.c. graduated stoppered cylinder, 4 c.c. of a saturated solution of sodium bicarbonate added, and the vessel shaken. A solution of potassium permanganate (25 grms. per litre) is added until, after shaking, the solution is tinted pink when 5 c.c. more are added. The cylinder must now be cooled to at least 10° C., 2 c.c. of carbon disulphide added, and then 5 c.c. of sulphuric acid, drop by drop, with shaking, care being taken to avoid a rise in temperature. The excess of permanganate is destroyed by careful addition of hydrogen peroxide. If the bromine content of the water is less than 5 times the iodine content, it does not interfere, and the iodine in the carbon disulphide is estimated by comparing the colour thus produced with that from a known amount of potassium iodide under the same conditions. If the amount of bromine is more than 5 times the amount of iodine, iodine bromide is formed. In that case some drops of 0·1 *N* potassium thiocyanate solution are added (an excess being avoided), which destroys the yellow colour of the iodine bromide, and the iodine can then be estimated as above. By this method 0·05 mgrm. of potassium iodide can be detected in the presence of 2000 its weight of potassium bromide. Chlorine does not interfere.

R. F. I.

Agricultural Analysis.

Method of Mineralogical Examination of Soils and its use in Determining Soil Types. J. Hendrick and G. Newlands. (*J. Agric. Sci.*, 1923, **13**, 1–17.)—Certain well-known English and Scottish soils have been subjected to mineralogical analysis which is shown to be of much utility in determining soil types. After the ordinary mechanical analysis the resulting "fine gravel," "coarse sand," and "fine sand," after ignition, are separated by flotation in bromoform (sp. gr. 2·9) into (*a*) the ferro-silicate group, which has density above 2·9, and the lighter portion of which floats on the bromoform; this portion is then separated by a mixture of bromoform and benzene of sp. gr. 2·65 into (*b*) the quartz group, which sinks, and (*c*) the orthoclase group, which floats. Each of the fractions is next passed under a powerful electro magnet which will pick out most of the iron-bearing compounds in each group. The different portions are then examined microscopically for the identification of the various minerals in the usual way. The finer portions obtained in the mechanical analysis are not suitable for mineralogical separation. Less importance attaches to the percentages of the different groups in the fine gravel and the coarse sand, as these contain many composite fragments, but the composition of the fine sand brings out the real significance of the origin of a soil. In the English soils examined the highest figure for the orthoclase group is at Woburn, where there is 6·2 per cent., whereas the lowest of the Scotch soils contained 13·4 per cent. (at Aulton), which is due to the fact that these soils have been derived from granitic rocks rich in felspar. On the other hand, the English soils are richest in the quartz group (Rothamsted has 95 per cent.), whereas the Scotch types contain 73 to 79 per cent. Soils of basic igneous origin are richest in the ferro-silicate group, and the Scotch and English soils show marked differences in the constituents of the group; in the latter, oxides of iron are more abundant, but the former contain larger proportions of biotite, hornblende and common minerals which are potential plant food. Details of the mineral constituents of thirteen soils are given. H. E. C.

Cause of the Toxicity of so-called Poisonous Greensand. J. W. Kelly. (*J. Agric. Research*, 1923, **13**, 223–228.)—Certain greensands in America, while valuable on account of their potash content, have been reported to be poisonous to plant life. Examination of these sands shows that they contain a large proportion of glauconite; this mineral yields much iron, aluminium and manganese when extracted by acid solvents, and it has been found that it is these elements in a form readily soluble in weakly acid media which are toxic to plants. The presence of lime prevents these toxic elements from passing into solution, so that those forms of greensand which contain shell-marl and other forms of lime are non-toxic. The addition of lime to the poisonous greensands inhibits their toxic action. H. E. C.

Colorimetric Determination of the Hydrogen-ion Concentration in Soils. C. T. Gimingham. (*J. Agric. Sci.*, 1923, **13**, 69–73.)—Although Fisher's method (ANALYST, 1921, **46**, 149) for the colorimetric estimation of P_H is satisfactory, there is often difficulty in obtaining a clear solution, and the more turbid the solution the less satisfactory is the result. The author uses the method of downward displacement and shows that by it a clear solution is readily obtained, and that the colorimetric estimation of the P_H on this solution, with the use of brom-cresol-purple as indicator, agree well with electrometric determinations. For the percolation the soil is packed to a depth of 8 to 10 inches in a glass cylinder (2 by 12 in.), fitted with a waxed cork and a short tube of about ½ in. diameter at the bottom; care is necessary in the packing, so that the water may run through at a suitable rate. Twice distilled water is run on to the soil, and the P_H determination is made upon the percolate, the first 50 or 100 c.c. of which is quite clear, as soon as sufficient volume has collected. The liquid should be protected from contamination by the laboratory air. H. E. C.

Estimation of Nitrates in Soil by the Phenol-Disulphonic Acid Method. C. T. Gimingham and R. H. Carter. (*J. Agric. Sci.*, 1923, **13**, 60–62.)—While confirming Emerson's method for the estimation of nitrates in soil (*Soil Sci.*, 1922, **12**, **413**), the authors point out that when the quantity of nitrate is small the results are irregular and low, owing to retention of nitrate by the filter paper. Of a number of filter papers tried, Whatman No. 1 is recommended as not retaining the nitrate; other grades of the same make give unsatisfactory results. The method used is as follows:—One hundred grms. of soil with a little precipitated calcium carbonate as flocculent, are shaken with 400 c.c. of water for 15 minutes, and allowed to stand, after which an aliquot part of the supernatant liquor is taken, flocculated with moist aluminium hydroxide and filtered through a coarse paper such as that mentioned. The precipitate and paper are well washed, and the nitrate estimated in the filtrate with phenol-disulphonic acid in the usual way. H. E. C.

Estimation of the Acids in Silage. E. Crasemann. (*Chem. Zeit.*, 1923, **47**, 134–135.)—The free volatile acids, combined volatile acids, and the total acids are estimated on a silage extract prepared by macerating for 12 hours 100 grms. of the sample with a litre of water, to which one c.c. of formalin may be added to inhibit bacterial activity. Such an extract gives the same result as the extract made by the boiling method described by Zeilsdorff and Benirschke (ANALYST, 1922, **47**, 529), but has the advantage that the solution is not so dark coloured. The total acids are estimated by diluting the extract with a large volume of water (free from carbon dioxide), and titrating, with the use of phenol-phthalein as indicator. For the estimation of the free volatile acids, which are chiefly acetic and butyric acids, the principle of Duclaux is adopted (*cf.* Wiegner and Magasanik, ANALYST, 1920, **45**, 24), based upon the fact that when a dilute solution containing acetic and butyric acids is distilled to half its volume the proportions of the two acids distilling over are 36·59 and 73·39 per cent. respectively. Three portions of 100 c.c. each are distilled from 200 c.c. of the extract with the addition of 100 c.c. of water between the distillations; the acidity of each fraction is separately estimated. As the third distillate consists almost entirely of acetic acid the residue in the flask will also contain acetic acid equivalent to $n \times 63{\cdot}41/36{\cdot}59$ c.c. of 0·05 N sodium hydroxide solution where n is the number of c.c. required for the titration of the third fraction. The combined volatile acids are similarly estimated after the addition of 10 to 20 c.c. of N sulphuric or phosphoric acid; the presence of these acids does not influence the acid content of the extract or affect the distillation constants. H. E. C.

Organic Analysis.

Quantitative Estimation of Carbon and Hydrogen in Organic Compounds containing Arsenic or Mercury. M. Falkov and G. W. Raiziss. (*J. Amer. Chem. Soc.*, 1923, **45**, 998–1003.)—Dennsted's method of combustion of organic compounds in a current of oxygen in presence of a platinum catalyst may be used for compounds containing arsenic if a boat containing red lead is placed in the combustion tube immediately after the boat containing the substance. The red lead reacts quantitatively with arsenic oxide, forming lead arsenate, which does not decompose at high temperatures, and may thus be freed, by continued heating, from any carbonaceous matter settling on it. For substances containing about 35 per cent. of arsenic, the red lead boat should be about 8 cm. long, and for those with higher arsenic content, from 10 to 11 cm. long. A piece of broken porcelain may be inserted in the tube after the red lead boat to prevent accidental deposition of particles of the red lead on the catalyst. The portion of red lead nearest to the catalyst is first heated with a Bunsen burner, the flame being moved gradually towards the other end of the boat as the combustion proceeds. Explosive compounds are mixed with sea-sand and analysed as Dennstedt directs.

When an organic mercury compound is to be analysed, a small boat, almost filled with a mixture of red lead and sea-sand, is inserted after the boat containing the substance, and is followed by a boat heaped up with silvered asbestos, so that the bore of the combustion tube is almost filled; this asbestos, however, must not touch the tube. The silvered asbestos is prepared by mixing purified asbestos with a solution containing 90 grms. of silver nitrate per 100 c.c., and evaporating to dryness on a sand-bath, the dried material being broken into pieces about the size of a pea, gradually heated to redness in a porcelain crucible, and stored over fresh calcium chloride. The mercury forms with the silver an amalgam unaffected by oxygen at comparatively high temperatures, and the increase in weight of the silvered asbestos represents accurately the weight of mercury in the compound analysed. Both the above methods yield satisfactory results. T. H. P.

Estimation of Sulphur in Organic Compounds. W. F. Hoffman and R. A. Gortner. (*J. Amer. Chem. Soc.*, 1923, **45**, 1033–1036.)—The method developed by Benedict (*J. Biol. Chem.*, 1909, **6**, 363) and Denis (*ibid.*, 1910, **8**, 401) for estimating the total sulphur in body liquids, especially urine, is applied by the authors to organic compounds in general. The reagent used contains 25 grms. of crystallised copper nitrate, 25 grms. of sodium chloride, and 10 grms. of ammonium nitrate, dissolved in sufficient water to make 100 c.c. of solution. From 0·1 to 0·2 grm. of the substance, depending on the sulphur content, is dissolved in an 11 cm. porcelain basin in a suitable solvent, such as alcohol, acetic or nitric acid, etc., and the solution evaporated almost to dryness on a water-bath. The residue is carefully ignited, finally at dull redness for a few minutes, and, when cold, dissolved in dilute hydrochloric acid, the sulphate being precipitated and weighed as barium sulphate in the usual way. A blank determination with the reagent is made in the same manner, and the results corrected accordingly. With a few compounds, some difficulty is encountered. β-Naphthalenesulphonamide requires heating with 10 to 15 c.c. of concentrated nitric acid until completely dissolved. Diphenylurea, after solution in alcohol and evaporation, leaves on the sides of the dish a gummy mass difficult to mix with the oxidising reagent; tribromothiophenol behaves similarly. Phenolsulphonephthalein must be dissolved in excess of sodium hydroxide solution. Thiophthalic anhydride gives low results, owing to its volatility, and sulphonal and trional give no sulphate for the same reason. The results obtained with proteins, which are dissolved in boiling hydrochloric acid, agree well with those yielded by fusion with peroxide. T. H. P.

Gravimetric Estimation of Organic Phosphorus. W. Jones and M. E. Perkins. (*J. Biol. Chem.*, 1923, **55**, 343–351.)—The various factors and reactions upon which the following method is based have been fully investigated, and it is shown that the precipitation of phosphoric acid by magnesia mixture is more accurate and more readily carried out in the presence of ammonium molybdate. In the estimation of phosphoric acid in solutions from which the usual ammonium molybdate separation is unnecessary the liquid is made alkaline with ammonia, 10 to 20 c.c. of 10 per cent. ammonium molybdate solution are added, and, after heating to 100° C., magnesia mixture is run in, drop by drop, with constant stirring. One-third of the volume of concentrated ammonium hydroxide solution is then added, and, after standing overnight, the coarsely crystalline heavy precipitate of magnesium ammonium phosphate is filtered off, washed and dried. The corresponding estimation of phosphoric acid in organic matter is preceded by the treatment of 0·3 or 0·35 grm. of the substance with 10 c.c. of sulphuric acid, 7·5 grm. of potassium sulphate and 5 drops of 10 per cent. copper sulphate solution, the mixture being heated until colourless as in Kjeldahl's method. The product is diluted to 200 c.c., treated with 4 grms. of ammonium nitrate and precipitated at

100° C. by the addition of 4 per cent. ammonium molybdate solution, the subsequent procedure being as usual. The magnesium ammonium phosphate thus obtained contains 6 molecules of water of crystallisation and is sufficiently pure for use as a standard for any of its constituents. On heating to bright redness for 1 minute it is converted completely into magnesium pyrophosphate. The maximum error obtained was −0·7 per cent. on the phosphoric acid present.

T. J. W.

Estimation of Formic Acid. E. O. Whittier. (*J. Amer. Chem. Soc.*, 1923, **45**, 1087.)—Jones (*Amer. Chem. J.*, 1895, **17**, 540) described a method for estimating formic acid by oxidation with standard permanganate in a solution made alkaline with sodium carbonate, the solution being subsequently made acid and mixed with excess of standard oxalic acid, and the excess of the latter determined by titration with permanganate. The author finds that this method only gives satisfactory results if at least 20 minutes is allowed for the completion of the oxidation. T. H. P.

Separation of Methyl Oleate and Linolate by Fractional Distillation. E. André. (*Comptes rend.*, 1923, **176**, 686–689.)—The separation of oleic and linolic acids by converting them into their methyl esters and subjecting the mixture to fractional distillation is tedious, and the polymerisation of the methyl linolate is a source of error. This is possibly preventable by addition of a small proportion of a phenolic compound, to act as an anti-oxidising agent (Moureu and Defraisse (*Comptes rend.*, 1923, **176**, 124). The only unsaturated fatty acids found by this method in grape-seed oil were oleic and linolic acids. T. H. P.

Inorganic Analysis.

Modification of Gillespie's Method for the Determination of Hydrogen-Ion Concentrations. W. D. Hatfield. (*J. Amer. Chem. Soc.*, 1923, **45**, 940–943.)—Gillespie's simple and accurate method for the colorimetric determination of hydrogen-ion concentration without the use of buffer solutions suffers from the drawback that the standards last for only a few hours (*J. Amer. Chem. Soc.*, 1920, **42**, 742). The rapid fading of the standards is due largely to a change produced in the hydrogen-ion concentration of the dilute acid and alkali solution by either atmospheric carbon dioxide or the action of the solutions on the glass of the test-tubes. For the production of the acid and alkaline colours the author replaces the dilute acid and alkali by roughly-prepared buffer solutions, addition of two or three drops of toluene to standards prepared with such buffers preserving satisfactorily all the indicators recommended by Clark, except methyl red; if, however, the methyl red standards are loosely stoppered for the first few days, before the stoppers are paraffin-waxed, the excess of toluene will evaporate. With the exception of methyl red, all the colour standards prepared as described below remain unchanged in tint for four to eight weeks, being kept in a dark cupboard when not in use.

When possible, the indicator concentrations recommended by Gillespie should be used, but with some of the indicators sold considerably higher concentrations are necessary to obtain good colour differentiation. The buffer solutions, made from ordinary chemically pure salts, are: I. *N* acetic acid (57·7 c.c. of glacial acetic acid diluted to 1000 c.c.) for the acid colours of bromophenol blue and methyl red. II. 7·0 grms. of potassium dihydrogen phosphate per 1000 c.c. of distilled water for the acid colours of bromocresol purple, bromothymol blue, phenol red, cresol red and thymol blue (alkaline range). III. 18·0 grms. of disodium phosphate decahydrate per 1000 c.c. of distilled water for the alkaline colours of bromophenol blue and methyl red, and also for bromocresol purple and bromothymol blue, if desired. IV. 1·0 grm. of anhydrous sodium carbonate per 1000 c.c. of distilled water for the alkaline colours of bromocresol purple, bromothymol blue, phenol red, cresol red, and thymol blue (alkaline range). The standards are made up in the manner indicated by Gillespie, but measurement ot the indicators and buffer solutions by means of drops, instead of c.c., is found to be very accurate and more convenient; the same drop-pipette should be used for both standards and solutions to be tested. T. H. P.

Electro-deposition Methods for the Estimation of Metals in Hydrochloric Acid Solution. A. J. Engelenburg. (*Zeitsch. anal. Chem.*, 1923, **62**, 257–284.)—The author has revised and modified the electrolytic methods of Schoch and Brown (ANALYST, 1912, **37**, 584) for the deposition of metals in the presence of hydrochloric acid. A platinum gauze cathode is used throughout, rotating at 800 to 1000 r.p.m.; after use it is cleaned off with nitric acid. For the estimation of tin, copper, antimony, bismuth and lead in their salts a quantity containing about 0·3 grm. of the metal is dissolved in 10 c.c. of hydrochloric acid, 2 grms. of hydroxylamine hydrochloride added, and the solution diluted to 200 c.c. for electrolysis. Tin is deposited in 35 minutes by a current of 1·5 amp. at temperature 35° C.; copper requires about 20 minutes at 70° C., and a cathode potential of 0·75 volt; antimony is completely deposited in 20 minutes at 50° to 70° C. with a cathode potential of 0·3 volt, bismuth requires the addition of a further 5 c.c. of hydrochloric acid, and is then deposited at the same temperature with a cathode potential of 0·5 volt; copper only requires 0·25 volt at the same temperature; in the case of lead the dilution is made with hot water and the deposition completed at 60° to 70° C. in 20 to 40 minutes by a current of 1·5 amp. The separation of cadmium from tin may be effected by depositing the tin first at 35° C. by a current of 1·5 amp. and cathode potential of 0·7 volt in half an hour; the cadmium is then deposited on another cathode by a current of 1 amp. at 55° to 70° C. For the separation of antimony and tin 15 c.c. of hydrochloric acid and 4 grms. of hydroxylamine hydrochloride are used in making the solution, and the antimony separated by a cathode potential of 0·28 to 0·35 volt at about 70° C., then the tin at 35° C. by a current of 1·5 amp. An alternative method for cadmium without the use of hydroxylamine consists in diluting a solution in 10 c.c. of hydrochloric acid to 20 c.c. passing a current of 1 amp. for 20 minutes, then adding 20 grms.

of ammonium oxalate and 10 grms. of oxalic acid to the solution, and depositing the cadmium by a current of 1·5 amp.; the time required is 40 minutes. When zinc is to be deposited the solution must only contain 1·5 c.c. of hydrochloric acid; the usual 2 grms. of hydroxylamine hydrochloride are added, and the deposition is brought about by a current of 4 amp. rising towards the end of the period of 15 minutes to 6 or 8 amp., the temperature being maintained throughout below 18° C. If cadmium is to be separated from the zinc, it is first deposited from the strongly acid solution, which is afterwards neutralised, and 1·5 c.c. of hydrochloric acid added before the cold deposition of the zinc, as above. Tin and lead may be similarly separated by using a current of 1·5 amp. Except in the case of lead, it is found that hydrazine sulphate may be substituted for the hydroxylamine as reducing agent; also that copper, tin and antimony, may be deposited in the presence of ammonium persulphate instead of a reducing agent, in which case there is the advantage that it is not necessary to measure the cathode potentials when a current of 1 to 4 amps. is employed. It is shown that metals can be detected qualitatively by measuring the cathode potentials of the solution; the characteristic values are:—Bismuth, −0·22; copper, −0·28; antimony, −0·36 to 0·38; tin, −0·58; cadmium, −0·77 to 0·82; and lead, −0·92 to 1·02 volt.

H. E. C.

Estimation of Lead Dioxide. C. R. Somayajulu. (*Proc. Sci. Assoc., Maharajah's College, Vizianagram*, Dec. 1922, 1–5.)—A mixture of 0·25 grm. of lead dioxide and 0·20 grm. of arsenic trioxide (accurately weighed) is gradually heated with 20 to 30 c.c. of 10 per cent. sodium hydroxide solution. When near the boiling point the liquid is stirred, the dioxide dissolving readily. Dilute sulphuric acid is cautiously added until a slight permanent precipitate is obtained. The solution is treated with excess of sodium bicarbonate, and titrated with 0·1 *N* iodine solution. The excess of arsenite over that required for the reaction $2PbO_2+As_2O_3=2PbO+As_2O_5$ is thus found (*cf.* ANALYST, 1922, **47**, 90).

W. R. S.

Systematic Method for Detecting the Principal Anions. L. Fernandes and U. Gatti. (*Gazz. Chim. Ital.*, 1923, **53**, I., 108–114.)—The substance is fused with sodium carbonate and the aqueous extract treated, drop by drop, with dilute acetic acid to decompose the excess of the carbonate and then rendered alkaline by addition of ammonia. The acids present are then precipitated in groups by successive treatment of the liquid with the following reagents: (1) Magnesium nitrate and ammonia: carbonic, phosphoric, phosphorous, arsenic, arsenious, hydrofluoric, silicic and hydroferrocyanic acids. (2) Calcium and ammonium nitrates: sulphurous, molybdic, tungstic, oxalic, tartaric and citric acids. (3) Barium nitrate: sulphuric, chromic and thiosulphuric acids. (4) Mercuric nitrate: hydroferricyanic and vanadic acids. (5) Silver nitrate: hydrochloric, hydrobromic, hydriodic, and thiocyanic acids. (6) The residual liquid is tested for hydrocyanic, boric, hypophosphorous, chloric, perchloric, nitrous, benzoic, and salicylic acids. A scheme is given for the analysis of each of the group precipitates. Tests for nitric, carbonic and acetic acids are applied to the original substance. T. H. P.

Precipitation of Platinum, Palladium, etc., with Thiocyanate. W. N. Iwanoff. (*Chem. Zeit.*, 1923, **47**, 209–210.)—The platinum chloride solution is evaporated twice with nitric acid, diluted to 0·25 per cent., heated to boiling, and precipitated gradually with a 0·25 per cent. solution of sodium thiocyanate (250 c.c. per 1 grm. of platinum). When precipitation is complete, 20 grms. of ammonium nitrate are added, and boiling continued for a few minutes. The voluminous black precipitate is left to settle, filtered off, washed, and ignited to metal. Iron and copper interfere. Palladium is precipitated more readily than platinum, but ignition of the precipitate furnishes fused metal containing 8 to 9 per cent. of sulphur. Rhodium is precipitated completely by sodium thiocyanate, provided an excess of the precipitant is avoided. The precipitation of iridium is unsatisfactory. W. R. S.

Separation of Acids in Aluminium Precipitates. A. Charriou. (*Comptes rend.*, 1923, **176**, 679–682.)—When aluminium is precipitated by ammonia from a solution of an alkali chromate, the precipitate remains yellow after filtration and washing, owing to the simultaneous separation of chromic acid in small proportions. Such chromic acid may be completely eliminated by washing the precipitate with 5 per cent. ammonium bicarbonate solution, which does not dissolve alumina in the cold; the bicarbonate retained by the precipitate volatilises on calcination

T. H. P.

General Method for the Detection of Volatile Acids. G. Karaoglanov. (*Zeitsch. anal. Chem.*, 1923, **62**, 217–222.)—The method is based on the strength and volatility of the acids when mixed with acetic acid. The solution containing the acid or salt is mixed with excess of 2 *N* acetic acid solution in a flask connected with two test tubes which contain the washing reagent appropriate for the identification of the particular acid. Air is aspirated through the mixture in the flask and through the liquid in the test tubes, with the result that the volatile acids pass over and are collected in the test tubes. The only acids volatile under these conditions are hydrogen cyanide, sulphide, sulphite, and nitrite, hypochlorous and carbonic acids. Ferro- and ferri-cyanides only give off hydrogen cyanide upon prolonged contact with the acetic acid. To detect sulphite in the presence of thiosulphate the liquid is much diluted, so that there is no precipitation of sulphur on mixing it with the acetic acid; then on aspirating air through the apparatus any discoloration of starch iodide mixture in the test tubes is an indication of the presence of sulphite; thiosulphate is then indicated by the precipitation of sulphur on the addition of a mineral acid to the acetic acid solution. If sulphide is also present, it is first removed by adding zinc chloride to the neutral solution and filtering off the precipitate, which contains the sulphide and which is subsequently identified by dissolving it in acetic acid and passing the volatile gas through lead acetate solution. To identify nitrite in the presence of nitrate, chlorate, and perchlorate, the mixture is treated as above, and the gas passed through diphenylamine solution, and hypochlorite may be detected in the presence of chlorate and perchlorate by means of a dilute solution of indigo. For the detection of cyanide in the presence of halogens and ferro- or ferri-cyanides, silver nitrate or a dilute solution of Prussian blue may be used. When two or more volatile acids are present they may be identified by arrangement of the reagents in suitable order; for cyanide and sulphite acidified silver nitrate and starch iodide are successively placed in the two test tubes; for cyanide and sulphide lead acetate and silver nitrate are used; for sulphite, cyanide and carbonate there are employed silver nitrate strong starch iodide solution, hydriodic acid (to remove the remnant of sulphur dioxide), and lastly barium hydroxide solution. If sulphide and thiosulphate are also present, zinc chloride is first added, and the carbonate, sulphide and cyanide are subsequently identified in the precipitate. H. E. C.

Qualitative Separation of Chloride Bromide and Iodide in Mixed Silver Halides. H. Schmalfuss. (*Zeitsch. anal. Chem.*, 1923, **62**, 229–231.)—The washed precipitate of the mixed silver halides is shaken with about four times its volume of a 15 per cent. solution of ammonium sesquicarbonate; this dissolves out the silver chloride, which may be reprecipitated, after filtration, by the addition of potassium bromide. The residue is then shaken up with hydrogen sulphide water and filtered, the filtrate, which contains hydrogen bromide and iodide, is divided into two parts; to the one part is added sodium nitrite and carbon disulphide, then a few drops of nitric acid, iodine being then indicated by a violet colour in the carbon disulphide; the other part of the filtrate is treated with chlorine water and shaken up with carbon disulphide, the iodine being thus oxidised and the presence of bromine shown by a yellow or brown colour in the carbon disulphide. If much iodine is present, the carbon disulphide layer containing it may be separated before the oxidation with chlorine water, and fresh disulphide then added. H. E. C.

Iodimetric Estimation of Sodium Hydrosulphite. (*Chem. Trade J.*, 1923, **72**, 224.)—The method is based upon the fact that sodium hydrosulphite in the presence of excess of formaldehyde breaks up into a mixture of sodium sulphoxylate-formaldehyde and sodium bisulphite-formaldehyde according to the equation:

$$Na_2S_2O_4+2CH_2O+4H_2O=NaHSO_2.CH_2O.2H_2O+NaHSO_3.CH_2O.H_2O,$$

and sodium sulphoxylate-formaldehyde reacts with iodine according to the equation: $NaHSO_2.CH_2O.2H_2O+2I_2=NaHSO_4+CH_2O+4HI$,
whilst sodium bisulphite-formaldehyde is unacted upon in neutral or acid solution.

Ten grms. of sodium hydrosulphite are added to 20 c.c. of 40 per cent. formaldehyde in distilled water, contained in a litre flask with the neck cut off to within 1 inch of the graduation mark, and the flask immediately corked. After thorough mixing, 20 c.c. of the solution are added to 100 c.c. of water in a beaker, and 50 c.c. 0·1 N iodine solution added. After standing for 2 minutes, the excess of iodine is titrated with 0·1 N thiosulphate solution. Then, if x c.c. of iodine solution are used, the percentage of hydrosulphite is $x \times 4{\cdot}352/2$. A correction must be applied for the loss of hydrosulphite due to oxidation by dissolved air and the small amount of air in the litre flask. A full description of this method of estimation may be obtained in leaflet form from Messrs. Brotherton and Co., Ltd., at their Port Sunlight Rainbow Works, in whose laboratory the method has been worked out. D. G. H.

Physical Methods, Apparatus, etc.

New Method of Micro-Sublimation. R. Kempf. (*Zeitsch. anal. Chem.*, 1923, **62**, 284–293.)—An apparatus is described and illustrated for the sublimation of quite minute quantities of substances on to microscope slides. It consists essentially of an electric heater so designed as to heat the sublimation chamber to any desired temperature, which is recorded on a thermometer, and to maintain it at that temperature for an indefinite period of time. There is also a tube by which the air in the sublimation chamber can be dried or can be replaced by an inert gas. With the use of this apparatus it is possible to detect as little as 10^{-2} mrgm. of caffeine, or 10^{-4} mgrm. of alizarin, or 6×10^{-4} mgrm. of arsenic. These substances and many others can be sublimed directly from mixtures containing them by heating at the appropriate temperature, and are then in a form convenient for the application of the usual micro-chemical tests. Human blood, when diluted 1:300 and sublimed at 90° C. for 20 hours, yields characteristic crystals which are of diagnostic value for the identification of blood stains on fabrics. The subliming temperatures and the crystalline form of the sublimates of a number of organic and inorganic substances are given. H. E. C.

Reviews.

ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION OF ORGANIC COMPOUNDS. I. M. HEILBRON, E. C. C. BALY, and A. W. STEWART. British Association Report, 1922, No. 12. Pp. 21. Price 1s. 6d.*

This report briefly outlines the energy quantum theory of Planck, and reviews the position of absorption spectra in relation to problems in chemical constitution and kinetics in the light of the experimental work done since 1920, in which year a report was last presented upon this subject (*B.A. Reports*, 1920, p. 222). There can be no doubt that the exact mathematical development of the theory of radiation has given a new impetus to research into chemical kinetics; the much clearer views which we now have of fundamental problems such as photosynthesis in plants, and the laboratory production of complex proteins and alkaloids by photosynthesis, show the large possibilities when research is guided by the quantum theory and carried out with great experimental skill.

The writers of this report provide us with a clear and concise resumé of the position of this subject up to its date, and one easily understandable by chemists

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* Obtainable from the offices of the British Association, Burlington House, London, W.1.

not well versed in higher mathematics. The first part deals with structures and changes of phase, and the second with the application of phases and radiation to reactions. With all its difficult points (and there are many, especially in connection with Einstein's photochemical equivalent), it is a theory of great heuristic value, and the only one extant to suggest a comprehensive explanation of homogeneous and heterogeneous catalysis, including the rôle of solvents. The report is, therefore, of much value in that it brings out the salient facts of the subject, eliminates matters of secondary importance, and shows the weighty evidence in favour of the phase theory, while admitting the weak points. The names of the authors are sufficient warranty of its thoroughness. H. E. Cox.

THEORIES OF ORGANIC CHEMISTRY. By F. HENRICH. Translated and revised from the 4th German Edition by Prof. T. B. JOHNSON and DOROTHY A. HAHN. Pp. xvi.+603. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1922. Price 30s. net.

From the point of view of the professional chemist, who is not unfamiliar with the outlines of the history of his subject, this translation will appear as an unusually useful and interesting summary of the very rapidly changing Theory of Organic Chemistry. It would probably appear of much smaller value as a work of reference, and is essentially a book requiring general study rather than a detailed consideration of its separate parts.

The translation has been very well done, both as regards freedom from error, and, more particularly, owing to the considerable improvements which have been introduced by the translators.

Among such small errors as there are, it may perhaps be mentioned that the second paragraph on page 180 appears to contradict the first paragraph on page 59, and that the stated dependency of "G," in the second paragraph of page 253, is confusing.

Not only has much of the matter been rearranged by the translators, with very great advantage, but what is probably the chief defect of the German edition —the lack of treatment of theories other than German—has been partly overcome by the inclusion of American work and thought.

It is hoped that in a subsequent edition, in continuation of this policy, and in spite of the very large amount of work always associated with such extensions of an existing book, the translators may see their way to describe at least outstanding advances made in other countries also, and so succeed in producing an ideally compact, historically treated statement of fundamental organic chemical theory as a whole. ARTHUR FAIRBOURNE.

SECOND YEAR COLLEGE CHEMISTRY. By WILLIAM H. CHAPLIN. Pp. 115. New York: John Wiley & Sons; London: Chapman & Hall. Price 7s. 6d. net.

This volume is intended as the laboratory companion of a text book by the same author. It is almost entirely quantitative in character, and the aspect is largely that of physical chemistry. Chapters are devoted to experiments on the gas laws, determination of combining, atomic and molecular weights, ionisation, chemical equilibrium of various types, and electro-chemistry. Sixty experiments in all are described, with adequate detail as to procedure; in many cases there is a wealth of detail which is, or should be, unnecessary for a student in his second year, and there is a distinct tendency thereby to cramp initiative and diminish self-reliance; on the other hand, however, the explanation of results is, in the main, left to the student, with the assistance of leading questions. The apparatus required throughout is inexpensive, simple, and such as can be fitted up without difficulty; it is clear that much time and careful attention have been devoted to the working out of this course.

The book contains a number of appendices which reveal the author's methods of laboratory organisation; these may be of use to teachers, but are somewhat out of place in a book to be issued to individual members of a class; two pages of logarithm tables are of doubtful value. The phraseology in some cases is not what is customary in this country.

A few of the experiments will prove useful in school work, and a further number in a university course, but the book as a whole does not seem likely to fill any gap in English educational practice. The printing, etc., are satisfactory in every way.

A. F. KITCHING.

OXIDATIONS AND REDUCTIONS IN THE ANIMAL BODY. By H. D. DAKIN, D.Sc., F.I.C., F.R.S. (2nd Edition). London: Longmans, Green & Co. Pp. ix.+169. Price 6s. net.

The study of the complex chemical changes within the human body, which precede or accompany the formation of carbon-dioxide and water, is as important to the physiologist as are those which concern the formation of the same products in the cylinder of the internal combustion engine. In both body and engine the air is the principle source of oxygen and the energy available for the production of work is dependent on the oxidation of carbon and hydrogen contained in complex chemical substances which constitute the greater part of the food in the one case and of the fuel in the other.

Of the two reactions that which takes place in the internal combustion engine is far the simpler, yet it is comparatively recent experimental work that has shown the beneficial effects following the injection of water before ignition, and much still remains to be learned of the part played by condensation on the surfaces of dust and other particles drawn into the cylinder with the mixture.

It is not surprising then that our knowledge concerning the oxidation and reduction processes in the animal body has been hard to win, and therefore, while we have progressed already further than the most optimistic would have cared to forecast a few years ago, the goal is not yet in sight. We know a great deal, as Dr. Dakin shows us in this book, concerning the intermediate stages through which fats, hydrocarbons, proteins and purins pass from their first entrance into the body as food to their final exit as excreta. We know much concerning the chemical systems (most of them reversible and due to the action of enzymes), by means of which one stage of synthesis or break-down is followed by its successor. But we have much to learn concerning the equilibria which exist between these bodies, and of the forces which induce the reactions to proceed in one direction in preference to another. Less still do we know of their velocities within the body or of the conditions which affect them.

The subject matter of the book divides itself into two parts, the first consisting of 25 pages only dealing with the nature of the oxidising and reducing agents of the body, and with the methods of investigation employed by the physiologist; the second and much larger part (120 pages) gives a separate chapter to carbohydrates, fats, proteins, purins, and miscellaneous organic compounds.

Dealing in turn with these two parts, we find in the introduction a statement of Wieland's hypothesis, which explains how it is that the presence of free oxygen is non-essential for oxidation processes to occur, so long as hydrogen acceptors, *e.g.* metallic palladium, are present instead. Thus, on shaking moist aldehyde in the absence of air with palladium black, acetic acid is formed, while the hydrogen liberated is found to become absorbed by the metal. This reaction, which proceeds rapidly at first, necessarily slows up as the palladium reaches saturation; but, by causing some other hydrogen acceptor to be present, at the same time (*e.g.* methylene blue) the reaction may go rapidly to completion. Turning to substances of physiological interest, Wieland found that glucose could be oxidised at low temperatures to carbon dioxide and water, using either atmospheric oxygen or quinones as acceptors for the hydrogen liberated. Similarly, lactic acid, phenols, etc., could be oxidised. But, probably, Wieland's most suggestive experiment was one in which alcohol was oxidised to acetic acid in the presence of quinone (or methylene blue) as hydrogen acceptor, using the acetic acid bacteria as catalyst in place of palladium. Of particular significance from the point of view of this hypothesis of Wieland's is the recent discovery by Hopkins of glutothione, a body found associated with actively living tissues, and which passes from the reduced to the oxidised form by a change involving essentially the loss of a hydrogen atom.

This oxidised form is of just the type required according to Wieland's hypothesis because its action as a hydrogen acceptor causes it to bring about various oxidation processes of which certain examples have already been mentioned above. The reduced form of glutothione thus produced can, in the presence of ordinary oxygen, form again the oxidised modification.

Hopkins found that the hydrogen ion concentration affected the change of the oxidised to the reduced form. In acid solution the system acts as a powerful hydrogen acceptor; in alkaline solutions it tends to unload hydrogen to other hydrogen acceptors, *e.g.* methylene blue. In fact, the system may be said to act as a co-enzyme, since it facilitates the oxidation of other constituents of the tissues.

It is of interest to physiologists to compare the effect of change of reaction on glutothione with that produced on hæmoglobin. An acid reaction tends to make hæmoglobin unload its oxygen to the tissues, and also to cause glutothione to take up hydrogen, *i.e.* both changes tend to facilitate tissue oxidation. In other words, since an acid reaction is brought about by tissue activity, the acceptance of hydrogen by glutothione under this condition is yet another reply to the demand of the tissues for oxygen.

It would seem proved beyond doubt, then, that for oxidations to occur in the body the paradox is true that, while oxygen is quite unessential, the presence of water is absolutely necessary.

As to the reaction of the oxidising agents found in the body, Dr. Dakin points out that some are autoxidisable, *i.e.* they become oxidised themselves to form substances possessing powerful oxidising properties. Thus, while an indigo blue solution is not oxidised by oxygen, it is readily attacked if benzaldehyde is present in the solution. Others, on the other hand, are peroxide-yielding substances, giving the characteristic reactions of hydrogen peroxide and bringing about *in vivo* similar reactions to those which this substance can perform *in vitro*. Of the latter, many examples are given—particularly striking being the oxidation of indol to indoxyl.

As to the nature of reducing agents found in the body but little is known. It would seem probable to the writer of this review that a great increase in our knowledge of these substances would follow the research work at present being carried out on "oxidation potential," which we shall look forward to reading in the 3rd edition of Dr. Dakin's book.

The author next describes the methods used by physiologists to determine firstly the end-products of oxidation and reduction processes in the body, and secondly the intermediate steps which lead to the production of a particular end-product. The end-products are, as a rule, easily estimated by feeding experiments, or better, by subcutaneous injection and subsequent analysis of the urine. Three methods of investigation are employed for determining the intermediate steps (*a*) by excluding in turn possible formulæ suggested as a result of experiments *in vitro*; (*b*) by administering to an animal the substance under investigation in quantities too large to be completely oxidised. In this way, beside end-products, intermediate products are also found in the excreta; (*c*) a method depending on the study of the oxidation and reduction processes effected by isolated surviving organs, *e.g.* the liver. Of all the parts of Dr. Dakin's book this appears to the writer to be the most interesting and the one worthy of much greater elaboration.

Turning now to the second part of Dr. Dakin's book, which deals with the oxidation of the different groups of organic substances of interest to the physiologist, we find in Chapter II. that fatty acids, both saturated and unsaturated, and those with branched chains, are dealt with. He concludes that part of the saturated undergoes oxidation by the successive splitting off of two terminal carbon atoms (the β-oxidation of Knoop), whereas another part becomes changed into unsaturated acids. Of the unsaturated he points out that, when oxidised, they yield products essentially similar to those derived from the corresponding saturated acids. They may also take up water to form optically active saturated hydroxy-acids, or they may undergo oxidation at the double linkage.

About the branched chain acids he concludes that they first tend to lose their side chains, and then proceed along similar lines to the first two classes above.

Chapter III. concerns the α-amino, α-hydroxy and α-ketonic acids, which are now, known to play such an important part in what may be called intermediary metabolism.

The α-amino acids are frequently converted into α-ketonic acids. The α-ketonic acid may be oxidised to a lower fatty acid which is then oxidised as described above, or it may be reduced either to a hydroxy-acid or to an amino-acid.

Chapter IV. deals with the carbohydrates, which, from the point of view of insulin alone, should amply repay a careful study. Recent work on sugars has shown their great structural complexity. Glucose, for example, consists of a mixture of at least two alkyl-glucosides in chemical equilibrium. Thus Nef and Glattfield found a hexose in alkaline solution to give a mixture of six isomeric hexoses, in addition to a mixture of sugars containing 2, 3, 4 and 5 carbon atoms. Of equal interest is the discussion of the probable precursors of lactic acid. Glyceric aldehyde, dihydroxy-acetone, and pyruvic aldehyde are all possible. Dr. Dakin discusses their rival claims with great clearness.

Chapter V. on purin derivatives, which remains practically unmodified from the previous edition, is followed by a very valuable bibliography, in which the references to each chapter are separately tabulated. H. HARTRIDGE.

THE CHEMISTRY AND TECHNOLOGY OF GLUE AND GELATIN. By R. H. BOGUE, Ph.D. Pp. 626. New York and London: McGraw-Hill Book Company. Price **$6.00.**

With the exception of the radio-active bodies, gelatin is perhaps the most interesting substance known. This may seem to be the prejudiced statement of a specialist, but it finds justification when the manifold usefulness of gelatin is considered. The gelatin jelly is the typical jelly, found in use as a food, in photography and photolithography, as a culture medium for bacteria, as membranes for ultra-filtration, etc., etc. Much of the importance of gelatin jellies is explained by Graham's discovery that, when not too concentrated, they allow almost unimpeded diffusion of electrolytes, conveniently combining the natures of liquid and solid. The first direct determinations of ionic mobilities by Lodge took advantage of this. The Liesegang phenomenon, usually demonstrated with gelatin jellies, has evoked a new interest in stratified minerals. Diffusion into jellies plays also a fundamental part in physiological processes and in tanning. Gelatin is the most effective protective colloid; hence its use in correcting cows' milk for infant feeding, and in preventing grittiness in ice-cream. As an emulsifier gelatin is much used in confectionery, in the preparation of horticultural emulsions, and in pharmacy. In chemistry, gelatin has been the material used in hundreds of researches on proteins, and the physical chemistry of acid and alkaline swelling (phenomena now amenable to quantitative treatment) will probably be the starting point for an understanding of the function of muscle, and is certainly the root of leather trades' science. The sewage disposal problem of a large American city has been solved by a direct application of results obtained from a study of gelatin swelling. The modern view of proteins as amphoteric bodies forming salts with acids or bases according to circumstances, but in harmony with well-established laws of chemistry, is a conception which may yet bridge the gulf between colloids and crystalloids. This is based upon work on gelatin by Pauli, Loeb and Procter, using the methods of physical chemistry. In a more or less degraded form, gelatin, as glue or size finds fresh uses as an adhesive in wood-working, book-binding, etc., as a sizing material for paper and textiles, as a binding material in the manufacture of matches, compositions, etc., as a main constituent in printing rollers and hektograph compositions, as a protective colloid in the electro-deposition of metals, ensuring the formation of smooth, hard, deposits, and as an ingredient in artificial ivory, mother-of-pearl, etc. Clearly a comprehensive work on gelatin and glues, giving due consideration to the scientific problems that arise, can hardly fail to be both interesting and important.

It may be said at once that Dr. R. H. Bogue, already favourably known as a research worker in this field, has produced such a book. As he states in his preface, previous writers of books have failed to be helpful on the *chemistry* of gelatin, though in extenuation it must be remembered that only within the last ten years or so has it become possible to clear one's ideas on the subject. Dr. Bogue has evidently worked through scores of recent papers on gelatin, and it is only in his book that the reader will find the discoveries of Pauli, Loeb, Procter, Sheppard and others brought together in an ordered way. He seems to prefer the views of Loeb to those of the Ostwald school, as is shown, *e.g.* in the discussion of the Hofmeister ion-series, but, as befits the present state of our knowledge, there is no rigid adherence to one mode of interpreting results. The day may come when, starting from the conception of gelatin as an amphoteric substance of high molecular weight, *i.e.* a complex polypeptide, we may be able to explain all its properties, colloidal and otherwise. But that cannot be done yet.

Dr. Bogue deals first with proteins generally, and then, in his second chapter, with the special chemistry of gelatin and its congeners. Succeeding chapters describe gelatin as a lyophilic colloid, and as an amphoteric colloid. The first chapter contains material familiar, no doubt, to many readers, but the others give information of which much is otherwise difficult of access. There are numerous references throughout the text. In criticism, it must be said that the treatment of the gelatin-tannin reaction is too brief, and also inaccurate. Most workers would prefer, in view of the constitution of the substances concerned, to speak of gelatin tannate rather than tannin gelatinate, and a statement attributed to Ricevuto is certainly wrong. The present writers cannot find support for it in Ricevuto's paper. J. T. Wood's important work on the reaction (*J. Soc. Chem. Ind.*, 1908, **27**, 384, 1164) appears to have been overlooked. In the sections on physical chemistry the importance of the Donnan equilibrium is clearly expounded, but some mention should have been made of it in the earlier section on osmosis (pp. 97–104), since determinations of the osmotic pressure of proteins mean nothing at all unless the equilibrium is taken into account. The discussion of the structure of gelatin solutions lacks reference to the work of Rohloff and Shinjo, Reiger, and Rankine, who showed that solutions of gelatin too dilute to set possess a small, but easily measurable form-elasticity, clear evidence of structure in such apparently perfectly liquid solutions. Dr. Bogue, however, has missed very little in the scattered literature on gelatin, and has ordered his matter in a very useful and readable manner.

Further chapters, forming Part II. of the book, are devoted to the following subjects:—Manufacture of glue and gelatin, water-resistant glues, glue and gelatin testing, analysis of gelatin, evaluation of gelatin and glue, and uses and applications of glue and gelatin. The account of glue manufacture (by Mr. R. C. Shuey) is the work of a thoroughly practical man, well versed in modern American methods, and thoroughly alive to the scientific aspects of the industry. The writers of this review, however, consider the chapter rather too short. It occupies only 47 of the 640 pages of the book. The manufacture of glue has certainly advanced very much in recent years through the adoption of spray and climbing film evaporators. When evaporation was not used, it was necessary to obtain more concentrated sizes by longer boiling, causing too great hydrolysis, and by avoiding too frequent changes of water, preventing complete extraction of the material. The Americans appear to pay more attention to thorough washing of the raw materials before boiling than is often done in England, but the addition of dry material to the pans, though useful in getting strong sizes, is very adverse to quality, since for rapid conversion of collagen into gelatin the raw material should be as thoroughly soaked with water as possible. The section on drying in "alleys" ("tunnels" in England) is very good and practical, and attention is directed to the often badly neglected questions of temperature and adequate air-supply. A method of preparing for boiling found by one of us to be very useful in certain cases is not mentioned in this chapter, and is possibly not known. Certain oily materials, such as seal-skin fleshes and ham-shanks that have been long exposed to the air, contain a quantity of oxidised fatty acids which emulsify very readily, and if these materials are delimed by acid, they give a very turbid and usually dark-coloured glue. If, however, after well liming, and washing free from loose lime, these materials are carbonated by blowing with carbon dioxide in a tank with water, the lime soaps are not decomposed, and a clear glue can be obtained, while the grease skimmed off the glue liquor is neutral fat, the lime soaps remaining in the scutch, from which they can be pressed after acid treatment.

The account of glue and gelatin testing and analysis is very full and detailed, perhaps in some places unnecessarily so. There are appendices on the determination of hydrogen-ion concentration.

It only remains to say that Dr. Bogue's book is much the best on the subject, and all chemists and technologists who have to deal with glue or gelatin are strongly urged to procure it.

H. R. PROCTER.
F. C. THOMPSON.