SEPTEMBER, 1932 Vol. LVII., No. 678

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Obituary

JOHN CLOUGH THRESH

THE passing of John Clough Thresh marks an epoch in English public health, for he was one of the early pioneers who established the importance of hygiene in connection with the home.

Thresh was born in Wakefield in 1850, and was educated privately and at Owens College, Manchester. His early interests were centred in pharmacy and chemistry, and resulted in his attaining the degree of D.Sc., London, in 1884. Later, at the relatively mature age of 39, he graduated in medicine at the Victoria University, Manchester, and in 1896 he was awarded the gold medal for his M.D. thesis. In 1892 he obtained the Diploma of Public Health of the University of Cambridge. He was a Fellow of the Institute of Chemistry, and had been a member of the Society of Public Analysts since 1894.

Although he published numerous communications and works on various problems of preventive medicine, and was the joint author of a useful manual on preservatives in food, his scientific publications were mainly concerned with water, and his "Examination of Water and Water Supplies" is regarded as a standard work in Great Britain, and, indeed, in all countries.

He also did much research on the purification of water and the effect of water upon health, the action of water upon lead and copper (see ANALYST, **1922, 47**, 459, 500; **1924, 49**, 124; **1925, 50**, 248), and various sterilisation processes, and, as a result of his experiments, the Excess Lime Process of Water Treatment was recently sanctioned by Parliament as an efficient method for the purification of river sources.

Dr. Thresh held many important appointments. He was the first Medical Officer of Health for the County of Essex, and occupied that position for 22 years, when he was appointed Consulting Medical Officer, a post he held until, 9 years ago, ill-health compelled him to resign. He was Lecturer in Public Health at

the London Hospital Medical College and Examiner in State Medicine for the University of London, and, in addition to his official appointments, he carried out an extensive consulting practice.

Dr. Thresh married in 1872, and his wife (who predeceased him) was a constant helpmeet throughout the course of a long life marked by intensive study, research and hard work. His home life was quiet and unostentatious, and those who were privileged to know him best fully realised his kindly nature and the many generous deeds which were done by him in the most unobtrusive manner.

His qualities of clear thought and capacity for hard work, coupled with his profound knowledge and experience, made Dr. Thresh in great demand as an expert witness in connection, principally, with questions relating to water supply, and his words always carried great weight with any Parliamentary Committee or Court before which he was required to appear.

All who have noted the remarkable changes in public health and in the prevention of disease which have occurred during the last fifty years will greatly deplore the death of one of the greatest pioneers in sanitary science and preventive medicine, and those who had the privilege of personal knowledge of Dr. Thresh will mourn the loss of a great teacher and the kindest of friends.

JOHN F. BEALE

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates

XXIII. The Quantitative Separation of Tantalum, Niobium, Titanium, and Zirconium, and a New Analytical Grouping

BY W. R. SCHOELLER, PH.D., AND A. R. POWELL

(Work done under the Analytical Investigation Scheme)

(Read at the Meeting, May 4, 1932)

THIS Section concludes the work begun in Section XV (ANALYST, 1929, **54**, 453), which dealt with the qualitative separation of these four elements. We may say at once that the pyrosulphate tannin method, which was shown in the earlier paper to be a very simple and effective procedure for the qualitative separation of the elements under discussion, is not here advanced for their quantitative separation. Whilst it proved invaluable for the quantitative recovery of small amounts of earth acid contained in titania precipitates, and in that rôle was incorporated in the perfected oxalate salicylate method (Section XXI, ANALYST, 1932, **57**, 74), it did not appear to lend itself in its original form to quantitative separations involving large quantities of earth acid. Fortunately, we were spared what would probably have proved a protracted investigation, by the discovery that our new tannin

method for the separation of titanium from zirconium (Section XVIII, ANALYST, 1930, **55**, 605) was capable of separating not only titanium, but also tantalum, and niobium from zirconium. This is not surprising, in view of the earlier application of tannin to the separation of the earth acids from zirconia (Section XIII, ANALYST, 1928, **53**, 517). Hence, the quantitative resolution of the ternary mixture (M_2O_5:TiO_2:ZrO_2) is accomplished by first eliminating ZrO_2, as shown in this paper; the binary mixture (M_2O_5:TiO_2) is then resolved into its constituents by the oxalate salicylate method (XXI, *loc. cit.*); finally, M_2O_5 is decomposed into Ta_2O_5 and Nb_2O_5 by the tannin method described in Section IV (ANALYST, 1925, **50**, 485).

TANNIN AS A GROUP REAGENT.—Important developments in the application of the procedure here discussed were forecast in Section XVIII. We found that the tannin process which separates titania from zirconia, will separate titania from thoria and alumina also, and we expressed the opinion that a separation of the earth acids from thoria and alumina by the same process would be feasible. This is now fully confirmed by experiment (*vide infra*); we are, therefore, in a position to make the following important generalisation:

Tannin quantitatively precipitates tantalum, niobium, and titanium from a barely acid oxalate solution half-saturated with ammonium chloride. Zirconia, hafnia, thoria, and alumina are not precipitated under those conditions. A quantitative separation of any (or all) of the precipitable, from any (or all) of the non-precipitable, elements can thus be achieved.

The practical importance of the new group-precipitation will be appreciated when it is realised that our procedure effectively eliminates from the solution the three elements chiefly responsible for the difficulties and complications peculiar to the analysis of earth-acid minerals. We propose using the following convenient terms:

Acid tannin group (or Group *A*): Ta_2O_5, Nb_2O_5, TiO_2.

Basic tannin group (or Group *B*): ZrO_2, HfO_2, ThO_2, Al_2O_3.

The oxides of group *A* are of more *acid* nature, and are precipitated by tannin from faintly *acid* solution. The oxides of group *B* are more *basic*, and are quantitatively precipitated by tannin from the oxalate solution when it is made faintly ammoniacal. Membership of group *B* is not confined to the four elements cited, as other metals of the "third" qualitative (ammonia) group—*e.g.* ferric iron, chromium, gallium—will be found to accompany alumina in the tannin separation from group *A*. Iron has not been included in this study because it can be precipitated as sulphide from tartrate solution, and thus be separated from all the earths. Uranium, another mineral associate of the earth acids, belongs to group *B*, as will be shown in a separate communication shortly to be published.

The analytical grouping of the rare earths as major constituents of a number of earth-acid minerals remains to be considered: they cannot be included in the present classification because their oxalates are insoluble in ammonium oxalate solution. In this connection, the work of Pied (ANALYST, 1925, **50**, 36) is being

re-investigated, and the conclusions will be published together with other necessary data on the determination of the rare earths in earth-acid minerals.

THE SEPARATION.—The method as described in Section XVIII was found to be applicable, with uniformly good results, to a variety of oxide mixtures (see Table). It aims at complete precipitation of the titania—or, in the present case, of group *A*—in one operation. The precipitate is dissolved and re-precipitated; the filtrates from both precipitates must be tested for complete precipitation. This is readily ascertained, thanks to the characteristic colour of the tannin complexes of group *A* (yellow tantalum, red niobium and titanium precipitates). The tannin complexes of group *B*, on the other hand, are dirty-white precipitates, easily soluble in dilute acid, and they become darker upon further addition of tannin and complete neutralisation.

Fractional Precipitation.—In Section XVIII the amount of tannin required for complete titanium precipitation is given as twelve times the weight of the titania. Now, if the addition of the reagent is purposely restricted (*i.e.* to 8 to 10 times the weight of group *A* oxides), the precipitation is incomplete, but the primary tannin precipitate TP^1, containing the bulk of group *A*, is free from group *B*. It is ignited and reserved as a final separation product.

The filtrate and washings from TP^1, boiled down to the original volume, are boiled, treated with 0·25 to 0·5 grm. of tannin, and titrated with *N* ammonia until the secondary precipitate, TP^{1a}, shows a dirty grey discoloration, which indicates incipient precipitation of group *B*. The ignited precipitate, TP^1, is re-treated as in Section XVIII; the resulting precipitate TP^2 represents the balance of group *A*. $(TP^1 + TP^2)$ is leached, ignited, and weighed as $(M_2O_5 + TiO_2)$.

The combined filtrates from TP^{1a} and TP^2 contain the oxides of group *B*, which are recovered, if desired, by boiling with more tannin and a moderate excess of ammonia (*cf.* Section XVIII, *loc. cit.*, and Section XIX, ANALYST, 1931, **56**, 308).

The above simple fractionation method yields one small intermediate fraction, the re-treatment of which in a smaller bulk of solution is more convenient and precise than that of the whole of group *A*. If group *A* is quite subordinate in the original oxide mixture, it is advisable first to produce the mixed precipitate TP^{1a}, and re-treat it, as is done in Method A, Section XIII (*loc. cit.*). The only difference between that method and the present one is, that the tannin precipitation is now carried out in a solution half-saturated with ammonium chloride.

RESULTS OF TEST ANALYSES.—The two tests Nos. 8 and 12 were published in Section XVIII, and are reproduced here. In Exps. 1 to 4 the composition of the oxide mixture was unknown to the operator. This practice had to be abandoned in the later tests because we were not then working together. The column headed "Tannin" gives the amount of precipitant used for the production of TP^1. The next two columns, headed TP^1 and TP^{1a}, respectively, give the *gross* weights of the two fractions. Where no weight is entered under TP^{1a}, the whole of group *A* came down in TP^1, slightly contaminated with group *B*, and the precipitate was accordingly re-treated as in Section XVIII. The result of the re-treatment of TP^1, or TP^{1a} (where such was obtained) followed by lixiviation of the final

precipitate TP^2 or combined precipitate ($TP^1 + TP^2$), is given in a single column headed "Final *P*."

Exp.	Group *A* Taken	Grm.	Group *B* Added	Grm.	Tannin Grms.	TP^1 Grm.	TP^{1a} Grm.	Final *P* Grm.	Group *A* Error Grm.
1	Ta_2O_5	0·1048	ZrO_2	0·1014	1·2	0·1072	—	0·1053	+0·0005
2	Nb_2O_5	0·1064	ZrO_2	0·1055	1·2	0·1054	0·0052	0·1062	−0·0002
3	Ta_2O_5	0·0672	ZrO_2	0·0890					
	TiO_2	0·0700			1·5				
	Σ	0·1372				0·1413	—	0·1368	−0·0004
4	Nb_2O_5	0·0515	ZrO_2	0·1486					
	TiO_2	0·0628			2·0				
	Σ	0·1143				0·1215	0·0060	0·1146	+0·0003
5	M_2O_5	0·0637	ZrO_2	0·1004					
	TiO_2	0·0551			1·5				
	Σ	0·1188				0·1259	—	0·1192	+0·0004
6	Ta_2O_5	0·1051	ThO_2	0·1042	1·0	0·1038	0·0017	0·1042	−0·0009
7	Nb_2O_5	0·1066	ThO_2	0·1028	1·0	0·0999	0·0077	0·1066	0·0000
8	TiO_2	0·0479	ThO_2	0·1068	0·8	(*a*)	—	0·0484	+0·0005
9	Ta_2O_5	0·0505	ThO_2	0·0818					
	TiO_2	0·0528			1·2				
	Σ	0·1033				0·1057	—	0·1023	−0·0010
10	Nb_2O_5	0·0628	ThO_2	0·0721					
	TiO_2	0·0433			1·2				
	Σ	0·1061				0·1055	0·0023	0·1059	−0·0002
11	Ta_2O_5	0·0551	Al_2O_3	0·2676					
	Nb_2O_5	0·0738			1·5				
	Σ	0·1289				0·1248	0·0068	0·1286	−0·0003
12	TiO_2	0·0532	Al_2O_3	0·2357	0·8	(*a*)	—	0·0528	−0·0004
13	Ta_2O_5	0·0613	Al_2O_3	0·1072					
	Nb_2O_5	0·0439			2·0				
	TiO_2	0·0534							
	Σ	0·1586				0·1584	0·0056	0·1587	+0·0001
14	Ta_2O_5	0·0431	ZrO_2	0·0567					
	Nb_2O_5	0·0303	ThO_2	0·0303	1·5				
	TiO_2	0·0380	Al_2O_3	0·0540					
	Σ	0·1114				0·1152	—	0·1112	−0·0002

(*a*) Not weighed

We submit that the tabulated results demonstrate the accuracy of the process, errors not exceeding 0·0005 grm. being recorded in 12 out of 14 tests. Further, the mode of working remained quite unaffected by the nature of the oxide mixture, which varied in composition in each experiment. The last test, involving six earths, was no more difficult than any of the tests with binary mixtures. We are not conscious of any exaggeration when we express the opinion that the process is one of the most remarkable yet discovered in the domain of the analytical chemistry of earth-forming elements. It owes its superiority to a combination of two factors: first, a clean-cut separation, based upon the more pronounced

differentiation in chemical behaviour between the two groups, brought about by the conversion of the earths into their oxalo-complexes; and secondly, the certain identification of tantalum, niobium, and titanium, by means of the characteristic colour of their tannin complexes.

SUMMARY.—Our recently-published method for the separation of titanium from zirconium, based on precipitation of the titania as tannin complex from the nearly neutralised oxalate solution half-saturated with ammonium chloride, has now been proved to afford a quantitative separation of tantalum, niobium, and titanium ("acid tannin group") from zirconium, thorium, and aluminium ("basic tannin group"). Under the conditions realised by the procedure, tannin acts as a group reagent, precipitating any or all of the members of the acid tannin group, and thus separating them from any or all of the members of the basic tannin group. The inclusion of certain other metals (*e.g.* uranium) in the last-named group is being investigated.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
ALDGATE, LONDON, E.C.3

A Rapid Method of Dissolving Lead Alloys Preparatory to the Determination of Tin and Antimony*

BY B. S. EVANS, M.C., PH.D., F.I.C.

WHEN a lead-tin alloy is once in solution in hydrochloric acid the determination of the tin is a relatively simple matter; in the absence of interfering metals it can be directly reduced, *e.g.* with metallic lead (A. R. Powell, *J. Soc. Chem. Ind.*, 1918, **37**, 287T), or with hypophosphorous acid (B. S. Evans, ANALYST, 1931, **56**, 171) and titrated.

To obtain the solution is, however, often a matter of considerable difficulty and delay. Finely divided lead alloys can be dissolved in a solution of bromine in hydrochloric acid; they must, however, be finely divided, as a very small lump of the alloy may delay solution for many hours; solution at best is slow, and all this time there is danger of loss of tin through volatilisation; in addition to this one can deal with only small samples.

In a former paper (ANALYST, 1927, **52**, 568) I published a method for solution of lead alloys, in lump form, in bromine with hydrochloric acid. This method would seem to constitute an advance, inasmuch as it enables one to deal with larger samples in lump form and, moreover, shortens the time required for solution; a serious drawback to it, however, is the somewhat complicated apparatus required. If we do not use hydrochloric acid as a solvent medium but try various mixtures containing nitric acid we are faced with a separation from the acid radicle; this, in itself, is no great difficulty (*cf.* B. S. Evans, ANALYST, 1932, 365), but, in addition,

* Communication from the Research Department, Woolwich

there is the trouble of finding an acid mixture which will dissolve both lead and tin. Quite a small quantity of hydrochloric or sulphuric acid in the solution mixture will practically stop solution altogether, owing to the deposition of the corresponding lead salt on the metal; on the other hand, if nitric acid is used, something must be added to prevent the formation of "metastannic acid," which, once formed, would be exceedingly difficult to get into solution again (methods, of course, exist in which the "metastannic" acid is filtered off and dissolved in strong hydrochloric acid, but there is considerable danger of losing tin in the process, and even so the solution occupies some time). I have used with great success a mixture of nitric with citric or tartaric acid for dissolving lead-antimony alloys (ANALYST, **1929, 54**, 404) and lead-tin alloys where the tin is present in small amount; where the amount of tin is higher, however, the amount of citric acid required to keep it in solution is prohibitive. Perchloric acid has come into prominence lately, chiefly in the United States, as a solvent for metals and an oxidising agent (*cf.* H. H. Willard and R. C. Gibson, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 88), and, as lead perchlorate is extremely soluble, it seemed worth while to try it as a solvent for the alloys under discussion. Lead itself dissolves rapidly and completely when the perchloric acid has become concentrated by evaporation; tin, however, and antimony form white insoluble compounds which are, apparently, of the nature of "metastannic" and "metantimonic" acids. On trying various mixtures of perchloric with other acids I found, for lead-tin alloys, that mixing perchloric acid with phosphoric acid gave a liquid with the desired properties. One final difficulty remained to be surmounted in that the tin seems to be converted into stannic chloride, and a considerable quantity of it was lost when solution was carried out in a beaker; this was overcome by carrying out the process in a flask fitted with ground-in tube acting as an air-condenser.

PROCESS FOR LEAD-TIN ALLOYS.—Details of the process are as follows:—A convenient amount of the sample (which may be in lump form) is placed in the flask; 15 c.c. of perchloric acid (60 per cent.) and 10 c.c. of syrupy phosphoric acid (these quantities are suitable for a sample weight of about 2 grms.) are heated in a beaker until dense white fumes appear; the beaker is then allowed to cool somewhat, and the acid mixture is poured on to the sample in the flask. The stopper carrying the condenser-tube is immediately inserted, and the top of the tube is closed with a rubber stopper carrying a glass tube connected by rubber tubing with a Mitscherlich absorption-tube containing 10 c.c. of dilute (1:1) hydrochloric acid. The liquid in the flask is now boiled gently until all the sample is dissolved; this usually takes from 10 to 15 minutes for a 2-grm. sample; if much tin is present, drops of stannic chloride can be seen condensing and running back into the solution, where apparently they react with the lead perchlorate, giving lead chloride; this lead chloride, not being on the surface of the metal, does not hinder solution in the slightest. When all the metal has been dissolved the apparatus is allowed to cool for some minutes, the bulb-tube is then detached, and the contents are poured into the reduction-flask of the tin titration apparatus described in former papers (Evans, ANALYST, 1927, **52**, 570; 1931, **56**, 172), and rinsed in with 10 c.c. of water; 30 c.c. of water are poured down the condenser-tube into the solution-flask, the apparatus being sloped and rotated meanwhile in order to rinse the walls; the

condenser is detached, and the stopper is rinsed into the reduction-flask with a little of a mixture of 70 c.c. of dilute (1:1) hydrochloric acid and 10 c.c. of dilute (1:3) sulphuric acid; the contents of the solution-flask are then poured into the reduction flask and rinsed in with the remainder of the acid mixture. Two or three grms. of sodium hypophosphite are next added to the solution, followed by 1 c.c. of saturated mercuric chloride solution, and the flask is shaken and warmed slightly; if the smell of chlorine persists, more hypophosphite is added in small amounts, followed by shaking and warming until the smell of chlorine is entirely dispelled; finally, 4 to 5 grms. of hypophosphite are added, and the stopper (with the titration attachments) is placed in the flask; carbon dioxide is passed through the flask for 10 minutes, the solution is boiled for 15 minutes (with carbon dioxide passing), and the liquid is cooled and titrated as previously described (Evans, ANALYST, 1931, **56**, 173). Some trials were made with weighed quantities of tin and lead, with the following results:

Tin taken Grm.	Lead taken Grm.	Titration c.c.	Tin found Grm.	Tin added Per Cent.	Tin found Per Cent.
0·100	1·90	16·95 of $N/10$	0·1007	5·00	5·03
0·080	1·92	13·50 ,,	0·0800	4·00	4·00
0·060	1·94	10·00 ,,	0·0594	3·00	2·97
0·040	1·96	6·80 ,,	0·0404	2·00	2·02
0·020	1·98	34·2 of $N/100$	0·0203	1·00	1·01
0·010	1·99	16·6 ,,	0·0098	0·50	0·49

The total time taken for a determination was about 80 minutes.

ANALYSIS OF LEAD-BASE WHITE METAL.—The above method of solution lends itself readily to the determination of tin in white metals containing a high proportion of lead. Trials were made on "White Metal A" of Messrs. Ridsdale's "British Chemical Standards." The composition of the alloy as given on the certificate is as follows:—Lead, 82·6; antimony, 12·04; tin, 4·64; copper, 0·33; iron, 0·06; bismuth, 0·03; arsenic, 0·06; zinc, 0·08 = 99·84 per cent.

In view of the presence of copper and of a very high proportion of antimony, a partial separation of the tin was required; the following method was adopted:—A sample-weight of 2 grms. was dissolved in the manner given above; the contents of the Mitscherlich tube and one 10 c.c. washing were poured down the condenser-tube, and the latter was rinsed down with 60 c.c. of dilute (1:1) hydrochloric acid and 20 c.c. of water. Without disconnection of the condenser tube the liquid in the flask was boiled for 10 minutes, then cooled and filtered, the precipitated lead chloride being washed with 100 c.c. of 15 per cent. hydrochloric acid. To the filtrate were added 30 c.c. of citric acid solution (100 grms. dissolved in 200 c.c. of water), followed by solid sodium hydroxide in small lumps until the maximum turbidity seemed to have been produced; then sodium hydroxide solution (20 per cent.) until alkaline to litmus and 50 c.c. in excess; finally, 10 c.c. of saturated potassium cyanide solution and about 5 grms. of sodium sulphide dissolved in water. The beaker was allowed to stand on the steam-bath for about 15 minutes, after which its contents were filtered and the precipitated lead sulphide was washed

with hot 5 per cent. ammonium chloride solution; 20 grms. of ammonium chloride and about 8 grms. of sodium hydrosulphite were added to the filtrate, which was then boiled for 1 minute, allowed to stand on the steam-bath for 10 minutes (with a further addition of 1 to 2 grms. of hydrosulphite), filtered hot, and the stannous sulphide precipitate dealt with as described in a former paper (Evans, ANALYST, 1932, 362). The results obtained from five determinations were as follows:

Found, 4·75, 4·69, 4·75, 4·75, 4·73; mean, 4·73 per cent.

Results of referee analysts given on certificate, 4·62, 4·94, 4·57, 4·74, 4·48, 4·67, 4·49, 4·86, 4·16, 4·83; mean, 4·64 per cent.

LEAD-ANTIMONY ALLOYS.—When the above method of solution was tried for lead-antimony alloys it quickly became manifest that something was wrong; the metal went into solution readily enough, giving a bright solution, but on attempting to determine the antimony in the solution by the bromate titration I invariably got low results. I next found that on re-reducing the same solution with sulphur dioxide and carrying through the titration afresh, I got rather higher, though still low, figures; a third titration gave results higher still, thus:

Lead taken Grm.	Antimony added Grm.	Antimony found	Grm.
1·90	0·1000	1st titration less than	0·0857
		2nd titration	0·0964
		3rd titration	0·0976

As it seemed evident that boiling with hydrochloric acid promoted better results, I treated a similar mixture in the same way, but boiled the liquid, after addition of hydrochloric acid, for half-an-hour before reducing; in this case I recovered 0·0994 grm. of the 0·1000 grm. originally added. The above figures, coupled with the fact that the product of heating such an alloy with a mixture of perchloric and phosphoric acids completely dissolves when boiled with water, seems to make it reasonably certain that antimony forms a complex with phosphoric acid, which is slowly and incompletely broken down by boiling with hydrochloric acid. This boiling with hydrochloric acid, besides giving results which were still somewhat low, seriously detracted from the value of the process by reason of the time taken up. In view of the fact that "metantimonic acid" is fairly soluble in hydrochloric acid which is not too dilute, I next tried eliminating phosphoric acid altogether and obtaining complete solution by boiling the product of the attack by perchloric acid with hydrochloric acid of approximately 1:1 strength; this modification at once proved satisfactory.

PROCESS.—The following process was worked out for 2-grm. samples; there is no reason to anticipate any trouble in using it for larger samples, but quantities, etc., and possibly the size of apparatus used might have to be modified. A suitable amount (*e.g.* 20 c.c. for 2 grms.) of perchloric acid is placed in a beaker and evaporated until the fumes given off become thick and heavy, somewhat resembling those obtained from sulphuric acid; the beaker is then allowed to cool somewhat. The weighed sample (which may be in lump form) is placed in the flask of the

apparatus, described for tin-lead alloys, the evaporated perchloric acid is poured on to it, and the condenser-tube is attached. The U-tube, described in the case of tin-lead alloys, was found to be not only useless, but a source of positive danger where antimony is concerned, owing to the extraction of antimony from the rubber stopper used to attach it to the condenser-tube; it has, therefore, been discarded. The flask is now heated until the sample has been completely attacked, the lead being in solution and the antimony in the form of a white precipitate; it is next allowed to cool sufficiently to admit of the safe addition of water, and 20 c.c. of water are run down the condenser-tube, followed by 100 c.c. of dilute (1:1) hydrochloric acid. The liquid in the flask is boiled under the condenser until all of the solid is in solution, after which it is transferred to a 750-c.c. flask and rinsed in with 200 c.c. of water. A rapid stream of sulphur dioxide is passed in for a minute or two, a fragment of broken pot is added, and the solution is boiled vigorously for 25 minutes, and is then titrated with bromate solution in the ordinary way. The whole process, from the time the sample is set to dissolve, can be carried out in less than an hour. It is advisable to put through a "blank" test on pure lead, as in the series given below a small blank was found; this blank was certainly not due to the methyl orange used, as at the end-point the colourless liquid can be strongly coloured by the addition of a further three drops of methyl orange solution, and this again completely discharged by one more drop of bromate. It seems probable that the blank is due either to the incomplete elimination of the last traces of the sulphur dioxide used or, much more likely, to traces of some relatively non-volatile sulphur compound carried over in the rush of sulphur dioxide gas. The following results were obtained by this method:

Lead taken Grms.	Antimony added Grm.	Titration 1 c.c. = 0·00308 Sb c.c.	Antimony found	
			Total Grm.	Corrected for blank Grm.
1·90	0·1000	32·60	0·1004	0·0998
1·92	0·0800	26·20	0·0807	0·0801
1·94	0·0600	19·60	0·0604	0·0598
1·96	0·0400	13·15	0·0405	0·0399
1·98	0·0200	6·60	0·0203	0·0197
1·99	0·0100	3·40	0·0105	0·0099
2·00	Blank	0·20		

I also determined antimony in the British Chemical Standards White Metal A, referred to above; the method used was exactly that given for lead-antimony alloys; the following results were obtained:

Weight of alloy taken Grm.	Titration 1 c.c. = 0·00308 gr. Sb. c.c.	Antimony found. Per Cent.
1·00	39·70 − 0·20 = 39·50	12·17
1·00	39·75 − 0·20 = 39·55	12·18
1·00	39·85 − 0·20 = 39·65	12·21
1·00	39·60 − 0·20 = 39·40	12·14

The results of the referee analysts given in the certificate were as follows:

12·02, 12·02, 12·00, 12·03, 12·2, 11·91, 12·02, 12·00, 12·1, 12·10 per cent.

In order to show that the tin present did not interfere with the titration I treated a mixture of 0·0800 grm. of antimony and 1·92 grm. of tin in the same way. In this case the large amount of white solid ("metastannic acid"?) took about 3 hours to dissolve completely in the hydrochloric acid subsequently added. The amount of antimony recovered was 0·0795 grm.

In conclusion, it may be as well to state that I have never noticed any tendency of the perchloric acid to explode under the conditions given above. Solution proceeds quite smoothly and normally, except for the formation of stannic chloride mentioned above. The concentration of the perchloric acid appears to play a considerable part in the rate of solution, which becomes rapid only when the acid is concentrated; this is the reason for the initial heating of the acid mixture, as it is undesirable to concentrate the acid to any great extent in presence of the sample, owing to the formation of the volatile stannic or antimonic chloride. Attempts were made to eliminate the condenser altogether in the determination of antimony, but this yielded low results.

Determination of the Sulphate Ion by Precipitation as Barium Sulphate

By J. NEWTON FRIEND, D.Sc., F.I.C., and W. N. WHEAT, B.Sc.

Apparently Fresenius (*Z. anal. Chem.*, 1870, **9**, 52) was the first to direct attention to the fact that barium sulphate, upon precipitation from solution, tends to carry down with it appreciable quantities of dissolved substances. This is particularly the case if barium chloride is used as the precipitant when determining the sulphate ion of salts of alkali metals. The occluded matter may then consist of barium chloride or alkali sulphate according to circumstances; if the former, the results are too high; but if the latter, they are too low (Allen and Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 588; Karaoglanov, *Z. anal. Chem.*, 1917, **56**, 417; Kolthoff and Vogelenzang, *Pharm. Weekblad*, 1919, **56**, 122). Röhrig (*J. pr. Chem.*, 1888, **37**, 225) was the first to record the absorption of lithium sulphate, and one of us (*J. Chem. Soc.*, 1929, 2330) found that the results with this salt may be several units per cent. in error. Being desirous of obtaining, if possible, accurate determinations of lithium sulphate we began this investigation.

Considerable difference of opinion has been expressed as to the manner in which impurities are retained by barium sulphate. Some attribute it to the formation of compounds such as $(BaCl)_2SO_4$ (Patten, *J. Amer. Chem. Soc.*, 1903, **25**, 186; Hulett and Duschak, *Z. anorg. Chem.*, 1904, **40**, 196), $K_2Ba(SO_4)_2$ (Kolthoff and Vogelenzang, *loc. cit.*) and $K_2[Ba_5(SO_4)_6]$ which Balareff (*Z. anorg. Chem.*, 1922, **123**, 69) claimed to have isolated. Others have suggested solid solution, the first to do so being Schneider (*Z. physikal. Chem.*, 1892, **10**, 425). Korte (*Trans. Chem. Soc.*, 1905, **87**, 1503), however, decided against this, and concluded that the action is partly chemical and partly physical, as previously suggested by Richards (*Z. anorg. Chem.*, 1902, **25**, 220). Many investigators now favour adsorption

(Weiser, *J. physical Chem.*, 1917, **21**, 214; Karaoglanov, *Z. anal. Chem.*, 1917, **56**, 225, 417; Chakravarti and Dhar, *Kolloid-Z.*, 1928, **44**, 63, and Balareff, *Z. anal. Chem.*, 1927, **72**, 303), a view that receives support from the electro-osmotic measurements of Mukerjee and Basŭ (*J. Indian Chem. Soc.*, 1926, **3**, 371), and from the observed general adsorptive power of precipitated barium sulphate (see de Brouckere, *Bull. Soc. chim., Belg.*, 1929, **38**, 409; 1930, **39**, 174). Further, microscopic examination shows that precipitated barium sulphate possesses fine capillaries, and adsorption of barium chloride in these may be so complete that a porous pot, in the pores of which barium sulphate has been precipitated, can function as a semi-permeable membrane with respect to solutions of barium chloride (Balareff and Kandilarov, *Z. anorg. Chem.*, 1927, **162**, 344). We have adopted the theory of adsorption as our guiding principle.

Two methods have already been recommended for making fairly accurate determinations of alkali sulphates. According to one (Richards and Parker, *Z. anorg. Chem.*, 1895, **8**, 413), excess of barium chloride is added, whereby the whole of the sulphate ion is precipitated as barium sulphate, the precipitate being contaminated only with barium chloride. After the precipitate has been ignited and weighed in the usual way the chloride is determined by fusion of the whole with sodium carbonate and determination as silver chloride. The equivalent amount of barium chloride is subtracted from the original precipitate, and the true amount of barium sulphate is obtained. This is too cumbersome for ordinary procedure. A second method consists in precipitating as barium sulphate under standard conditions and applying an empirical correction (Winkler, *Z. angew. Chem.*, 1920, **33**, 59, 159, 162; Allen and Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 588). The principle of this method cannot be regarded as satisfactory.

Adopting the view that contamination of the precipitate is due essentially to adsorption, we hoped it might be possible to remove adsorbed material by a simpler method than that of Richards and Parker by modifying the conditions in accordance with recognised principles for avoiding adsorption in general.

As theory demands, adsorption by barium sulphate is reduced by precipitation in extremely dilute solution (Hahn and Otto, *Z. anorg. Chem.*, 1923, **126**, 257), whilst prolonged standing is found to reduce the amount of adsorbed alkali sulphate (Allen and Johnston, *loc. cit.*; Johnston and Adams, *J. Amer. Chem. Soc.*, 1911, **33**, 829). When precipitated very slowly at 100° C. barium sulphate may be obtained very free from contamination by using a diffusion method extending over several days (Johnston and Adams, *loc. cit.*).

We find that very satisfactory results can be obtained with lithium sulphate in solutions containing no other dissolved substances by adopting the following precautions:

(1) The concentration of the alkali sulphate should not exceed about 0·01 grm.-mol. per litre.

(2) The solution—conveniently about 350 c.c.—is acidified with hydrochloric acid, the concentration of which is best kept near $N/100$, since barium sulphate is appreciably soluble, even in dilute acid (Sjollema and van't Kruys, *Chem. Weekblad*, 1907, **4**, 589; Jensen, ANALYST, 1928, **53**, 136).

(3) The solution is now heated to boiling, and a dilute solution of barium chloride is added dropwise, with constant stirring, until about twice the amount of barium chloride theoretically necessary for precipitation has been added. This ensures complete precipitation of all the sulphate ion (see Richards and Parker, *loc. cit.*). The low results in experiments 15 to 18 (see Table) are in part attributable to insufficient excess (10 per cent.) of barium chloride.

(4) The solution is kept near the boiling-point for ten minutes and is then allowed to stand over-night. Immediate filtration was found to yield somewhat erratic results, probably because equilibrium had not been established. Sometimes the weight of precipitate was greater upon immediate filtration than upon standing (expts. 5, 6), but usually less (expts. 7 to 10, 11 to 14, and 15 to 18), probably in part because of the greater solubility of the precipitate in hot than in cold solution, for the liquid that had stood for some time was always filtered cold.

No.	Volume of solution c.c.	Normality of HCl	Excess of $BaCl_2$ added Per Cent.	Duration of standing before filtration Days	Nature of filtration	Anhydrous lithium sulphate Taken Grm.	Anhydrous lithium sulphate Found Grm.	Error Per Cent.
1	200	*N*/100	100	1	Cold	0·2688	0·2701	+0·48
2	"	"	"	5	"		0·2689	+0·04
3	200	2*N*	100	1	Cold		0·2687	−0·04
4	"	"	"	5	"		0·2702	+0·52
5	400	*N*/10	100	Nil	Hot		0·2698	+0·37
6	"	"	"	6	Cold		0·2688	0·00
7	200	*N*	100	Nil	Hot		0·2660	−1·04
8	"	"	"	Nil	"		0·2633	−2·04
9	"	"	"	14	Cold		0·2716	+1·04
10	"	"	"	14	"		0·2706	+0·67
11	100	*N*	120	Nil	Hot	0·3935	0·3959	+0·61
12	"	"	"	Nil	"		0·3962	+0·69
13	"	"	"	14	Cold		0·3976	+1·04
14	"	"	"	14	"		0·3985	+1·27
15	400	*N*/10	10	Nil	Hot		0·3782	−3·89
16	"	"	"	Nil	"		0·3805	−3·31
17	"	"	"	1	Cold		0·3858	−1·96
18	"	"	"	1	"		0·3856	−2·01
19	350	*N*/100	100	1	Cold*	0·3875	0·3885	+0·26
20	"	"	"	1	" *		0·3893	+0·46
21	350	*N*/20	100	1	Cold	0·3875	0·3872	−0·08
22	"	"	"	1	"		0·3874	−0·03
23	350	*N*/100	100	1	Cold		0·3873	−0·05
24	"	"	"	1	"		0·3879	+0·10
25	"	"	"	1	"		0·3874	−0·03
26	"	"	"	1	"	0·3552	0·3548	−0·11
27	"	"	"	1	"		0·3552	0·00

* 40 minutes' heating only (p. 562)

(5) After standing, the clear, supernatant liquid is decanted through a filter as completely as possible, some 350 c.c. of distilled water are added to the barium sulphate, and the whole is heated for not less than two hours in a water-bath, with frequent stirring. This process, which serves to remove most of the remaining

adsorbed material, was not done in expts. 1 to 18. Expts. 19 and 20 indicate that 40 minutes' heating is insufficient for this purpose. The solution is now cooled, the supernatant liquid is filtered off, and the precipitate is washed into the filter with a minimum quantity of hot water. By filtering in the cold, any correction for the solubility of barium sulphate is rendered negligibly small.

(6) The filter paper is dried, the precipitate is detached and transferred as completely as possible to a porcelain (not platinum) crucible, the paper being incinerated separately and the ash arranged on one side of the crucible. After the ignition a drop of dilute sulphuric acid is added before the final heating and weighing (Acree, *J. Biol. Chem.*, 1906, **2**, 135; Pellet, *Ann. Chim. Anal.*, 1907, **12**, 186, 318; Truchot, *ibid.*, 1907, **12**, 267; Folin, *J. Biol. Chem.*, 1907, **3**, 83).

The results obtained in this investigation are summarised in the table. Expts. 21 onwards were carried out according to the method outlined above. Spectroscopic examination of the ignited precipitates showed that traces of the alkali metals were still present. Nevertheless, the results are as concordant as is usually required in ordinary quantitative analysis.

We desire to thank Mr. R. H. Vallance for carrying out some analyses to check the above results.

THE TECHNICAL COLLEGE,
BIRMINGHAM

The Water-Protein Ratio of Lean Meat, and Its Bearing upon the Analysis of Sausages

BY F. W. JACKSON, B.Sc., A.I.C., AND OSMAN JONES, F.I.C.

(*Read at the Meeting, April* 6, 1932)

THE Meat Rationing Order, 1918, (No. 404) of the Ministry of Food, fixed the minimum quantity of meat in sausages as 67 per cent. for first quality and 50 per cent. for second quality. When the Order came into force it was necessary for analysts to employ some suitable method for the determination of the percentage of meat in sausages, a point which hitherto had received little attention.

In the ANALYST for April, 1919 (**44**, 125, 127), two methods were published, one by George Stubbs and Andrew More, and the other by A. W. Stokes. Both methods were based upon the average percentage of water and nitrogen in de-fatted meat. Stokes assumed that all meat contained on the average 70 per cent. of water, and based his calculations upon this figure. Stubbs and More worked upon varying water-protein ratios for de-fatted meat according to the kind present. For pork they used 3:1; for beef, 3·26:1; and for mixed meats, 3·13:1.

According to Moulton (*Meats through the Microscope*, University of Chicago Press, pp. 320, 321) the water-protein ratio for the composite lean flesh of pork (118 samples) is 3·4:1, and for composite beef flesh (34 samples) it is 3·6:1. The

figures show that the water-protein ratio varies, not only for different kinds of meat, but also for different "cuts" of the same meat.

We obtained the following figures in the analysis of samples of meat, which may be regarded as representing the average quality used by reputable manufacturers of sausages.

TABLE I

SAMPLES OF PORK

As much as possible of the external fat was removed prior to the analysis of the samples, so that the samples can be regarded as lean meat as commonly used in sausage manufacture.

Description of sample	Fat Per Cent.	Mineral matter and undetermined substances Per Cent.	Water Per Cent.	Protein (N × 6·25) Per Cent.	Water-protein ratio
Gammon	2·87	1·05	73·97	22·11	3·35:1
Gammon	5·01	1·23	72·20	21·56	3·37:1
Gammon	9·21	1·33	68·78	20·68	3·32:1
Gammon	3·41	1·20	73·08	22·31	3·28:1
Back	10·19	1·10	69·59	19·12	3·43:1
Back	26·23	1·30	55·33	17·14	3·17:1
Back	6·18	1·52	69·11	23·19	2·98:1
Shoulder	26·00	1·08	58·42	14·50	4·09:1
Shoulder	43·36	1·27	41·81	13·56	3·08:1
Shoulder	2·18	1·07	75·66	21·09	3·59:1
Shoulder	7·49	1·21	68·87	22·44	3·07:1
Mixed	1·46	1·34	75·90	21·31	3·56:1
Mixed	2·86	1·18	73·40	22·56	3·25:1
Mixed	5·52	1·26	74·40	18·82	3·95:1
Mixed	4·39	1·43	72·84	21·34	3·42:1
Mixed	4·80	1·56	73·77	19·87	3·71:1
Mixed	2·36	1·51	76·06	20·07	3·79:1
Mixed	—	—	75·32	21·83	3·45:1
Mixed	—	—	76·66	19·93	3·85:1
Mixed	—	—	75·11	20·25	3·71:1
Mixed	—	—	77·68	20·06	3·87:1

Average water-protein ratio .. 3·4:1

SAMPLES OF BEEF

As much as possible of the external fat was removed prior to the analysis of the samples, so that the samples can be regarded as lean meat as commonly used in sausage manufacture.

Description of sample	Fat Per Cent.	Mineral matter and undetermined substances Per Cent.	Water Per Cent.	Protein (N × 6·25) Per Cent.	Water-protein ratio
Bull.					
Round	0·69	1·96	75·34	21·91	3·44:1
Flank	2·04	1·02	75·92	21·02	3·62:1
Shoulder ..	1·08	0·95	76·68	21·29	3·60:1
Shoulder	2·01	0·97	75·31	21·71	3·47:1

TABLE I—SAMPLES OF BEEF—*continued*

Description of sample	Fat Per Cent.	Mineral matter and undetermined substances Per Cent.	Water Per Cent.	Protein (N × 6·25) Per Cent.	Water-protein ratio
Bullock.					
Flat rib	5·21	0·90	73·79	20·10	3·67:1
Shoulder ..	11·05	0·80	68·93	19·22	3·59:1
Sticking—					
neck end ..	3·02	0·89	76·03	20·06	3·79:1
shoulder end ..	3·02	1·44	76·40	19·14	3·99:1
centre	4·76	0·91	74·01	20·32	3·64:1
neck end ..	2·05	0·91	76·99	20·05	3·84:1
Mixed	1·31	1·08	75·96	21·75	3·49:1
Clod	—	—	76·97	19·75	3·90:1
Flank	—	—	68·84	20·71	3·30:1
Veal	2·20	1·22	76·80	20·78	3·70:1

Average water-protein ratio .. 3·6:1

SAMPLES OF PORK (FAT)

The samples can be regarded as "fat" as commonly used in sausage manufacture.

Description of sample	Fat Per Cent.	Mineral matter and undetermined substances Per Cent.	Water Per Cent.	Protein (N × 6·25) Per Cent.	Water-protein ratio
Gammon	89·87	0·08	8·34	1·71	4·80:1
Gammon	93·32	0·07	4·86	1·75	2·70:1
Back	92·75	0·10	5·72	1·43	4·00:1
Back	93·48	0·06	5·53	0·93	5·94:1
Shoulder	90·73	0·12	8·10	1·05	7·71:1
Shoulder	90·50	0·09	7·08	2·43	2·91:1

Average water-protein ratio .. 4·2:1

It should be observed that the average figures closely approximate to those given by Moulton (*vide supra*).

We have found that the water-protein ratio varies in individual carcases. It is obviously impossible to establish an average water-protein ratio which will cover all classes of meat, such as offal, cured meats, pickings and canned meats, as well as the better-class "cuts." Indeed, it is not necessary because, with the possible exception of the very cheapest grade of sausages, manufacturers in this country have other outlets for odds and ends of meat.

An examination of the data given in Table I leads to the conclusion that the various water-protein ratios used by Stubbs and More need some modification, and that more accurate ratios would be:

Water-protein for fresh pork ..	3·4 : 1
Water-protein for fresh beef	3·6 : 1
Water-protein for fresh mixed meats	3·5 : 1

Since in most cases the analyst will not know the kind of meat which has been used in the article which he has under examination, he will of necessity have to adopt the mixed meat ratio of 3·5 : 1. It is only in special cases that the other ratios will be applicable.

When canned meat is re-canned after being mixed with other materials, as is sometimes done, the water-protein ratio may vary within such wide limits that it is not desirable to base the analysis of such a mixture upon the scheme now under discussion.

As no regulations at present exist in this country governing the meat percentage in sausages (the Meat Rationing Order, 1918, No. 404, having lapsed after July, 1920), it is probable that the determination of the amount of this product in such articles is not so important as at one time, but it is nevertheless of considerable importance to those engaged in fulfilling the conditions laid down in government and public institution contracts.*

It must be admitted that the *accurate* determination of the percentage composition of such articles as sausages is not practically possible at the present time; such factors as the varying water-protein ratio in meats, the kind and age of the meat used, the nature of the "filler," the nitrogen content of the "filler," the water associated with the filler, and the amount of "added water," all tend to render the final result inexact, but we feel that a nearer approximation to the correct composition of meat and cereal mixtures, such as sausages, will be obtained by using the modified water-protein ratios suggested.

The data given in Table II refer to samples of sausages of known recipe, and show the percentage of meat, as determined by the use of Stubbs and More's water-protein ratio and of the new ratios now proposed.

If reference be made to our data given in Table I, it will be observed that the ratios for fat are more variable than those for lean meat, and were it possible to eliminate some, or all, of the other errors which inevitably arise in the examination of sausages (see above), it would be necessary to take into consideration this variable ratio; but, unless the percentage of fat is abnormally high, the correction

* Regulations regarding the composition of sausages in some foreign countries and British Possessions are as follows:

Holland	Sausages to be labelled with statement showing the percentage composition.
Belgium	Starch not to exceed more than 5 to 8 per cent. No statement is made with regard to percentage of added water.
Brazil	No cereal matter allowed.
France	Meat content is not fixed, but no offal may be used, and the water must not exceed 75 per cent. of the fat-free product.
U.S.A.	Sausages shall not contain cereal in excess of 2·0 per cent.
Canada	Not more than 60 per cent. of water or 5 per cent. of cereals. There must be no added water.
N.S. Wales S. Australia Tasmania Queensland Victoria N. Zealand S. Africa Straits Settlement	75 per cent. of meat. Not more than 6 per cent. of starch.

which would need to be applied would have no material effect upon the accuracy of the calculated results.

TABLE II

PORK SAUSAGES	Percentage of meat as calculated on Stubbs and More's water-protein ratio 3·0:1	Percentage of meat as calculated upon water-protein ratio 3·4:1	Percentage of meat according to recipe
Sample No. 1	Lean meat .. 33·0	Lean meat .. 36·7	Lean meat .. 49·5
	Fat .. .. 29·8	Fat .. .. 29·8	Fat .. .. 16·2
	Total meat .. 62·8	Total meat .. 66·5	Total meat .. 65·7
Sample No. 2	Lean meat .. 22·3	Lean meat .. 24·6	Lean meat .. 30·8
	Fat .. .. 26·5	Fat .. .. 26·5	Fat .. .. 19·6
	Total meat .. 48·8	Total meat . 51·1	Total meat .. 50·4
Sample No. 3	Lean meat .. 36·8	Lean meat .. 40·3	Lean meat .. 44·8
	Fat .. .. 23·4	Fat .. .. 23·4	Fat .. .. 21·0
	Total meat .. 60·2	Total meat .. 63·7	Total meat .. 65·8
Sample No. 4	Lean meat .. 41·8	Lean meat .. 45·9	Lean meat .. 50·4
	Fat .. .. 22·8	Fat .. .. 22·8	Fat .. .. 21·0
	Total meat .. 64·6	Total meat .. 68·7	Total meat .. 71·4
BEEF SAUSAGES	Water-protein ratio 3·26:1	Water-protein ratio 3·6:1	Recipe
	Lean meat .. 21·9	Lean meat .. 23·6	Lean meat .. 30·5
	Fat .. .. 26·6	Fat .. .. 26·6	Fat .. .. 19·6
	Total meat .. 48·5	Total meat .. 50·2	Total meat .. 50·1
MIXED MEAT SAUSAGES	Water-protein ratio 3·13:1	Water-protein ratio 3·5:1	Recipe
	Lean meat .. 35·4	Lean meat .. 38·5	Lean meat .. 39·1
	Fat .. .. 19·8	Fat .. .. 19·8	Fat .. .. 19·6
	Total meat .. 55·2	Total meat .. 58·3	Total meat .. 58·7

Note.—In practice the so-called "lean" meat always contains a considerable amount of fat, and the fat meat some water and connective tissue, so that it is not possible for the analytical findings for lean and for fat to agree with the amounts of these substances shown by the recipe, but the total meat as determined should, of course, show a close approximation to the quantity which has been put in.

In determining the ash of the sample considerable difficulty may be experienced in removing all the carbon without using a high temperature. We have found that in some cases it is desirable to ascertain the total percentage of salt in the sample and that remaining in the ash, so that necessary adjustment can be made for the amount of salt which has volatilised at the high temperature used. Alternatively, the ignition may be conducted at a low temperature, such as that given by an Argand burner.

The practical work involved in the determination of the data given above has been considerable, and most of it has been carried out by Messrs. T. G. Joyce, B.Sc., F.I.C., H. Firth, F.I.C., J. W. Black, B.Sc., A.I.C., and B. Gough, and we are indebted to these gentlemen for the very real help given, with regard to both the work and the suggestions made.

The Determination of Meta- and Ortho-Cresols in Mixtures of Cresols

By C. EDWARD SAGE, F.I.C., and H. RONALD FLECK

The preparation of synthetic resins involves the employment of phenols in large quantities, and the short range of boiling points between ortho-, meta- and para-cresols does not permit a complete separation, by commercially possible methods, of fractional distillation. In consequence of this, the meta-cresol, which is essential for satisfactory resin synthesis, is usually obtained mixed with varying proportions of its isomers.

Potter and Williams have recently suggested for the determination of ortho-cresol (*J. Soc. Chem. Ind.*, 1932, **51**, 60T) the employment of a modification of Cocking's method (Analyst, 1920, **45**, 370), in which they make use of cineole in the reverse way to that employed for the determination of cineole in essential oils containing that substance.

Their published results indicate that they have made experiments with mixtures of cresols, and found the cineole products afford useful indications of the amount of the ortho-compound in commercial cresol, but we have carried the work a stage further by determining the freezing-points of the cineole complex with a larger range of mixtures.

The results recorded below indicate that the method is applicable to mixtures containing from 15 to 100 per cent., and that lower percentages can be estimated by mixing with an added known weight of pure ortho-cresol in the same way as Cocking determines the percentage of cineole in oils containing small proportions, by adding a known amount of cresineol and making allowance for it in calculating his results.

The method usually employed for the evaluation of cresol with respect to the meta-compound was introduced by Raschig, and has appeared in the last two editions of the German Pharmacopoeia (D.A.B.5 and 6). It involves the treatment of the cresol mixtures with sulphuric and nitric acids in order to produce tri-nitro-meta-cresol, the other cresols being oxidised and, under the conditions of the test, yielding no weighable crystalline material.

Several difficulties arise when dealing with cresol in this way, and the results of the test include very big allowances for loss during the process.

It takes a long time to perform the operations, and these are not free from danger. The cresols containing low percentages of the meta-compound yield tars and other inconvenient products, and eventually a mixture of nitro-compounds with an indefinite melting point; all of these difficulties render the method unsatisfactory.

The yield on which calculations are based is liable to considerable variation, and it is assumed, if 10 grms. of a sample of cresol yield 8·7 grms. of tri-nitro-meta-cresol, that 50 per cent. of actual meta-compound was present, these figures

being far removed from the theoretical ones which might be expected when working with pure compounds.

A consideration of these facts showed the desirability of a more accurate and rapid method of estimation, and this has been worked out for mixtures of the three isomeric cresols, and it is hoped to extend the scope of the method to commercial cresylic acid. The method depends on the formation of an insoluble resin with formaldehyde in alkaline solution. It was found that ortho- and meta-cresols gave such a resin, whilst the para-compound did not.

By determination of the combined ortho- and meta-cresols in a given sample by formation of the aldehyde resins, and deducting from the result the amount of ortho-compound found by the cineole method, an approximately accurate estimate of the amount of meta-cresol can be ascertained.

The method has been verified on many mixtures of known composition, the materials used being pure cresols, the physical constants of which had been carefully ascertained.

The mean of the results of a number of determinations by means of the pure compounds has suggested a reasonably accurate factor for converting the weight of cresol resin into the weight of cresol, and this is the same for ortho- and meta-cresols. The maximum deviation experienced in obtaining this factor was $\pm 0{\cdot}1$ per cent., and the mean value of the results showed that 1·33 grm. of the resin is equivalent to 1 grm. of either ortho- or meta-cresol.

The resin, obtained in the manner described hereafter, is of a pale cream colour and friable, and decomposes slowly on prolonged heating, formaldehyde vapours being evolved.

METHOD.—About 3 to 4 grms. of the cresol mixture are accurately weighed into a 50-c.c. measuring flask, and made up to the mark with a 10 per cent. aqueous solution of sodium hydroxide. The determination is made in duplicate with two portions of 10 c.c. each. These are pipetted into 100-c.c. Erlenmeyer flasks, 5 c.c. of water and 5 c.c. of 40 per cent. formaldehyde solution are added to each, and the reaction mixture is heated for exactly 5 minutes in a boiling water-bath.

The mixture is cooled and acidified with 20 c.c. of concentrated hydrochloric acid, being meanwhile vigorously shaken and kept cool. The large excess of hydrochloric acid is necessary in order to obtain the condensation product in an easily filterable form. The mixture is allowed to stand for about two hours at room temperature, then filtered on to a Gooch crucible, or on counter-poised filter papers. The resin is washed with cold water until free from chlorides, after which it is dried for exactly one hour in a water oven at 98° to 100° C., and then allowed to stand over concentrated sulphuric acid in a desiccator. The drying at 100° C. must not be prolonged, as the precipitate has a tendency to decompose.

The weight of resin, multiplied by 0·752, gives the weight of ortho- and meta-cresols in the mixture, and when the amount of ortho-cresol, found by the freezing-point method, is subtracted from the total, the remainder will be the amount of meta-cresol. The mean of two determinations should be taken.

FREEZING-POINT METHOD.—The mixed cresols (2·1 grms.) are placed in the inner tube of a standard crystallising-point apparatus. Into this is weighed 3 grms. of pure cineole, the mixture is stirred, and the freezing-point is taken when the temperature of the mixture just remains constant. The crystals are re-melted, and the freezing-point observed several times. The mean value of the results is taken after omitting the first result, which is usually low.

The standard mixtures of ortho-cresol used were prepared from the pure substance, pure meta- and para-cresol being used as the diluent. If the ortho-cresol is low in amount, the mixture can be enriched with a known weight of ortho-cresol, and allowance made for this.

TABLE I

Taken				Found		
m-Cresol Per Cent.	*o*-Cresol Per Cent.	Freezing-point °C.	Weight of resin from 1 grm. of mixture Grm.	*m*-Cresol Per Cent.	*o*-Cresol Per Cent.	Error Per Cent.
45·6	40·5	29·8	1·0193	45·1	40·8	−1
29·8	39·2	28·5	0·9177	29·5	39·5	−1
30·0	62·0	40·0	1·2236	30·2	62·0	+0·7
39·8	30·6	24·0	0·9363	39·7	30·6	−0·3
52·2	29·0	22·5	1·0800	52·3	28·7	+0·2

If no other phenols are present, the difference may be taken to be para-cresol.

TABLE II

Standard mixtures of ortho-cresol with meta- and para-cresols

o-Cresol, per cent.													
100	95	90	85	80	75	70	65	60	55	50	40	30	20
Freezing-point of the cineole compound, °C.													
55·2	53·5	51·7	49·6	47·7	45·6	43·6	41·4	39·1	36·8	34·2	29·5	23·6	14·6

THE LABORATORIES,
10, LONDON ST., E.C.3

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.

NOTES ON THE HORTVET CRYOSCOPE

THE Hortvet Cryoscope may be made more practical by the introduction of the following adjustments:

(1) LEAKAGE OF ETHER.—The apparatus, as supplied, allows ether vapour to escape at many points. The cork is very porous and may be treated with a thick mixture of gum and French chalk, which dries to a hard surface, effectually preventing leakage. Any similar ether-insoluble mixture would serve the purpose. Leakage between the nickel screw-cap and the body of the container is stopped by the use of several wide rubber bands. The exit tube for the ether vapour

leads into an open tube with a side-tube at the base. It is preferable to replace this with a plain tube with rubber bung fitted with inlet tube and outlet tube, the latter conveying the vapour by means of rubber tubing and glass tube to the grating of the sink. The smell of ether will then be imperceptible.

(2) METHOD OF STIRRING.—The ebonite top of the stirrer has a hole through the centre; the top is unscrewed, and a stout thread is passed through the hole, the thread being jammed as the ebonite is screwed into position. The thread passes through a stout wire ring fitted in the hole at the top of the thermometer, and on the end of the thread is tied a hinged nickel ring (such as is used in loose-leaf books). The thread is of the length most convenient for working. A steady vertical pull is obtained. The stirrer is raised at each stroke to a height sufficient to ensure complete stirring of the sample, and this point may be determined by noting the figure on the thermometer to which the top of the stirrer must be raised so that the wire ring of the stirrer reaches the surface of the liquid. When the thermometer and stirrer are removed for cleaning purposes the hinged ring is opened and attached to the ring at the top of the thermometer.

(3) PARALLAX.—The magnifying glass supplied is unnecessarily large, does not magnify greatly, and is awkward to use. This glass and the rod to which it is attached may be removed by unscrewing the nut under the wooden shelf through which the rod passes. A thermometer magnifier (Gallenkamp), consisting of a clip holding an object glass, gives a better magnification, and by a simple device parallax can be avoided. On the far lens of the object glass are placed in line, and wide apart, two small black dots, and on the near lens one black dot near the centre. The reading is taken by moving the clip on the thermometer until the three dots and the top of the mercury column are in line. A slight up or down movement of the head will throw the dots out of alignment. It is only necessary to clip this attachment to the thermometer when a reading is to be taken.

(4) ICE.—It is often a matter of difficulty to obtain a supply of ice just when it may be required. At the front of the apparatus there is a metal socket, the use of which is not explained in the literature supplied with the apparatus. This may be conveniently used to obtain the small particle of ice necessary for each experiment. The starter is placed in a narrow glass tube with sealed end and flanged top, the tube being slightly wider than the starter and containing sufficient water just to cover the hole in the side of the starter, air bubbles being excluded. When the temperature of the control thermometer falls below 0° C. the cork is removed from the socket, and the tube containing the starter (and fitted with a rubber collar to prevent loss of ether vapour) is inserted in the socket. The water is "encouraged" to freeze, as the temperature falls, by manipulating the starter at intervals. When the temperature reaches the required point the tube is taken out and the starter withdrawn by a slow firm twisting movement and quickly placed in the sample. Any excess of ice on the starter may be removed by means of a wooden mallet. Some practice is required to avoid breaking the tube when withdrawing the starter, but the tubes are easily and quickly made if this should occur.

LAG.—It is very important to tap the thermometer sufficiently long after the mercury appears to have reached its highest point, in order to obtain a correct reading.

DOUGLAS HENVILLE

THE DETECTION OF RECONSTITUTED MILK

ACTING on information that reconstituted milk was being made and sold as milk by a wholesaler in the district, an inspector visited the premises and took samples. There was a box of dried milk in the yard, together with three churns—one

containing milk, one containing cream, and one containing reconstituted milk, which, according to the vendor, was to be used in making cheese. No cheese or boards, cloths, etc., for making cheese were to be found, but it was denied that reconstituted milk was being sold as milk. Samples of each on analysis gave the following figures:

	Fat Per Cent.	Solids-not-fat Per Cent.
Cream	50·2	3·9
Milk	6·98	8·25
Reconstituted milk	0·85	20·62

It was doubtful whether the sample of milk did or did not consist of reconstituted milk. According to the Dried Milk Regulations, dried skimmed or dried machine-skimmed milk is dried milk containing less than eight per cent. of milk fat. The sample of reconstituted milk was, therefore, probably made from dried skimmed milk containing between 3 and 4 per cent. of fat.

At this time two samples of milk obtained in the ordinary course of sampling were found to contain excessively high percentages of solids-not-fat, and both these samples had been supplied to the retailers by the vendor of the reconstituted milk referred to above. It was also reported from a neighbouring borough that milk containing excessively high solids-not-fat was being supplied by the same wholesaler. At this period there was a scarcity of milk. In appearance these samples could not be distinguished from natural milk; they were apparently made from dried skimmed milk by admixture with water and cream and then pasteurised.

There is the same difficulty in detecting this product as there is in the case of artificial cream. The test for nitrates might in both cases give information. If the reconstituted milk is made to contain the normal amount of fat and solids-not-fat, this test might not be made on an apparently genuine milk. A positive nitrate test given by such a milk would indicate the possibility that the sample contains reconstituted milk. D. R. Wood (ANALYST, 1932, 247) mentions a sample of unwatered milk which contained a considerable amount of nitrate. Hortvet freezing-point determinations were carried out on the samples, and the following results were obtained:

		Fat Per Cent.	Solids-not-fat Per Cent.	Acidity, as lactic acid Per Cent.	Freezing-point °C.
1	Milk from yard	6·98	8·25	0·27	—0·580
2	Retail sample A ..	3·30	9·45	0·15	—0·600
3	Retail sample B ..	3·20	9·60	0·16	—0·606
4	Reconstituted milk from yard	0·85	20·62	0·42	—1·398
5	Milk taken on delivery at the request of the wholesaler from the retailer of sample B	3·10	8·75	0·15	—0·551

All the above samples were fresh when the tests were made, so that the acidity was not due to sourness. The acidity of a reconstituted milk will depend upon the amount of dried milk used, and where the solids-not-fat of the product is high the acidity of the depression of the freezing-point will also be increased.

A. van Raalte (ANALYST, 1929, **54**, 266) states that a freezing-point lower than —0·59° C. must be considered as unsatisfactory, and that the milk obtained from cows with diseased udders can have a freezing-point below —0·57° C. Monier-Williams, however (*Food Reports*, No. 22), states that "however abnormal the sample from a chemical point of view, the freezing-point seems to be almost unaffected."

Freezing-point determinations were made on solutions of dried milk of varying strengths prepared in the laboratory. The solutions were prepared by weighing the dried milk in the freezing-point tube, thoroughly mixing with warm water, cooling, and making up with water to the required weight. No. 1 was made with distilled water, and Nos. 2 and 3 with tap-water. The freezing-point of the tap-water supplied to the laboratory is —0·019° C.

	Solids-not-fat Per Cent.	Freezing-point °C.
Solution 1	8·37	—0·510
,, 2	8·83	—0·550
,, 3	9·54	—0·605

As would be expected, the depression of the freezing-point increases with the content of solids-not-fat. Reconstituted milk made from the brand of dried milk used and containing a normal content of solids-not-fat shows a normal depression of the freezing-point. A high solids-not-fat figure, together with a greater depression of the freezing-point, indicates the possible presence of reconstituted milk. A sample of milk low in solids-not-fat and showing, by a positive nitrate test and a lessened depression of the freezing-point, the presence of added water, may consist of watered milk, or reconstituted milk low in solids-not-fat. The nitrate test would not, of course, be of use in districts where the water used in the manufacture of the milk is free from nitrates.

As Section 4 of the Milk and Dairies (Amendment) Act, 1922, prohibits the sale of milk reconstituted from either dried or condensed milk, dilutions of unsweetened evaporated milk were also tested.

	Fat Per Cent.	Solids-not-fat Per Cent.	Ash Per Cent.
Evaporated milk, Brand A	9·26	22·19	1·89
,, ,, ,, B	9·31	22·99	1·93
,, ,, ,, C	9·10	22·56	2·17

		Solids-not-fat Per Cent.	Freezing-point °C.
Brand A.	Dilution 1	8·37	—0·515
	,, 2	8·90	—0·553
	,, 3	9·54	—0·596
Brand B.	,, 1	9·22	—0·573
Brand C.	,, 1	9·03	—0·624
	,, 2	9·03	—0·623

The results obtained in the case of dilutions made from Brand A and Brand B are of the same order as those obtained from the dried milk. The experiments made with two separate dilutions of Brand C show a considerably increased depression of the freezing-point. It will be noted that the analysis of this brand shows the highest percentage of ash.

Legal proceedings were taken against the vendors of the two samples of milk containing 9·45 per cent. and 9·60 per cent. of solids-not-fat, respectively. In each case the summons was dismissed without costs. In a similar case at Battersea (an account of which was published in the local press) the analysis of the milk showed normal figures. It was, however, admitted by the firm concerned that the milk was made from dried separated milk, mixed with cream and water, and homogenised. It was stated that the milk was supplied only to people who knew of what it was composed. The summons was dismissed under the Probation of Offenders Act, with two guineas costs.

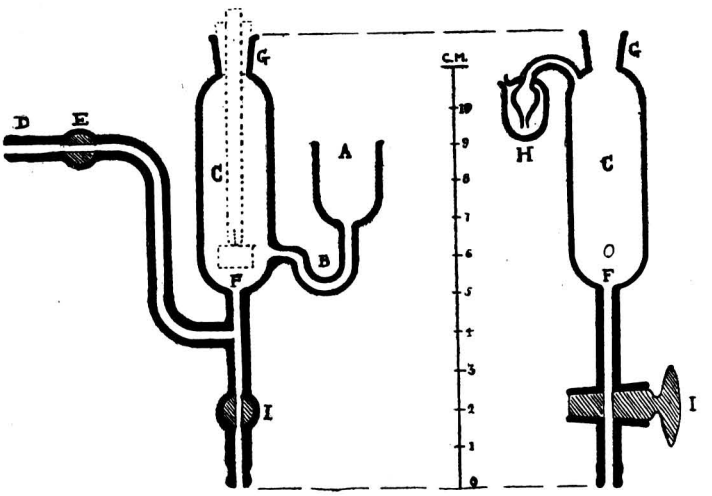
STEPNEY BOROUGH LABORATORY,
43, WHITE HORSE STREET, E.1

DOUGLAS HENVILLE

A HYDROGEN ELECTRODE VESSEL

MANY hydrogen electrode vessels have been described, but very few of them are suitable for the rapid repetition of measurements with moderate quantities of liquid. To ensure speed in use the vessel should be made as small as is convenient, and should be totally enclosed, so that the time of saturation is short. The introduction of the liquid under examination should be possible without undue re-assembly of parts, and the solution should be removable and the vessel capable of being washed out without dismantling the electrode system.

The Clark rocking electrode (*J. Biol. Chem.*, 1915, **23**, 475) has all these advantages, but requires the use of expensive shaking apparatus and a complex junction vessel. The vessel here described and shown in the scale drawing has the advantage of simplicity.



The funnel limb, A, serves as a funnel for filling and washing out the vessel, and also as a connecting-tube for the reference half-cell. The U-bend, B, acts as a trap to prevent diffusion of the junction liquid into the main vessel, C. The hydrogen stream enters at D, is controlled by the stopcock E, and finally bubbles into the vessel at the orifice, F, which is two to three mm. in diameter. The platinum electrode is supported in the neck, G, by means of a rubber stopper, and the hydrogen escapes from the trap H. When the determination is complete, the stopcock I is opened and the liquid run away to waste. The vessel is washed out by filling the funnel, A, with water, and then flushing away by opening the stopcock, I. Saturation is usually complete in three minutes, and tests can be repeated with great rapidity. The amount of solution used for each determination is five to seven ml. Temperature measurements of the solution can be made by inserting a thermometer into the funnel, A.

The vessel has been in use in this laboratory for a considerable time, and has proved satisfactory for rapid routine determinations.

The author wishes to acknowledge the permission of Messrs. Baird & Tatlock (London), Ltd., to publish this description, and to thank Dr. Sand, of the Sir John Cass Technical Institute, for his interest in the work.

ARTHUR J. LINDSEY

THE LABORATORY,
BAIRD & TATLOCK (LONDON), LTD.,
CROSS ST., HATTON GARDEN, LONDON, E.C.1

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.

MISDESCRIPTION OF BATH SALTS

ON June 21st, a tradesman was summoned, under the Merchandise Marks Act, at Woolwich Police Court for selling, under a false trade description, a packet of bath salts. Evidence was given that the defendant had sold the packet for 2d., and that its contents, when analysed, were found to consist of 97·8 per cent. of ordinary salt, with 2·2 per cent. of moisture and impurities.

The Stipendiary Magistrate (Mr. Metcalfe) said that he was satisfied that the defendant sold the salt under a false trade description. He regarded the case as very serious, and imposed a fine of 40s.

Department of Scientific and Industrial Research

FOOD INVESTIGATION

THE FREEZING, STORAGE AND TRANSPORT OF NEW ZEALAND LAMB*

THE introduction to the Report deals with the scientific basis of the freezing, storage and transport of frozen mutton and lamb. Autolysis is so slow, even at the freezing-point of meat, that its effects may be ignored. Micro-organisms which can cause spoilage, either by decomposition of the flesh by the enzymes they produce, or by the absorption, particularly by the fats, of the nauseous products of their metabolism, are not very active at temperatures below freezing, and, even on frozen meats, growth is restricted almost entirely to yeasts and moulds. Probably growth ceases at about −8° C. Changes in the fat are due either to hydrolysis, in which the glycerides are partly broken down to the corresponding fatty acids and glycerol without change in flavour (ANALYST, 1931, **56**, 748), or to oxidation, when lower fatty acids and aldehydes giving an unpleasant taste are produced. Both changes were very slight in carcases held at −10° C. for 18 months, and oxidation was much below that necessary to alter flavour (ANALYST, 1931, **56**, 538). During storage at temperature constantly below −8° C., changes affecting the physical properties of consistence and appearance, but not, so far as is known, the dietetic value of the meat, may occur. The work on fish at the Torry Research Station (ANALYST, 1931, **56**, 531) may mean that storage at much lower temperatures (−20° C.) is advisable from this point of view.

The object of the present Survey was to secure accurate data concerning temperature, relative humidity, and movement of air throughout each stage from the abattoirs in New Zealand to the wholesale markets in Great Britain, and to correlate these data with the appearance of the meat and its loss in weight. Part I deals with the analysis of the physical conditions, including cooling floors, freezing

* Special Report No. 41, by E. Griffiths, J. R. Vickery, and N. E. Holmes. Obtainable at Adastral House, Kingsway, W.C.2. Price 7s. 6d. net.

chambers, cold stores in New Zealand, and transport from stores to ship. The materials used for thermal insulation are described, and the use of self-contained refrigerating plants for rail and road vans is discussed. Overseas transport, transport from the docks to the cold stores, and a summary, with comparisons of the total losses in weight, conclude Part I.

Part II deals with the effects of environment on the quality and appearance of New Zealand mutton and lamb. It is emphasised that loss of bloom of carcases of lamb during storage is approximately proportional to the extent of the evaporation of water from them. Loss of bloom may result from an increase in the opacity of the connective tissue or skin covering the carcase owing to excessive drying of the superficial muscles, or from chemical changes of the red muscle pigment haemoglobin to the brown oxidised methaemoglobin. Such changes may be prevented or minimised by not allowing sweating in contact with the outer air; by storage at a constant temperature and high humidity at or below $-8°$ C., and by storage at very low temperatures.

The general conclusions and recommendations of the Report include many suggestions for improvement at the various stages. It is noted that the average total loss of weight during cooling; freezing; 28 days' storage in New Zealand; ocean transport, and 28 days' storage in Great Britain, as determined for 657 carcases of prime quality, was 3·65 per cent., and was slightly greater for second-quality lamb.

D. G. H.

BUILDING RESEARCH

DETERMINATION OF FREE CALCIUM OXIDE AND HYDROXIDE.*

THIS publication is a small-scale treatise on the determination of the calcium in calcareous building materials which is present as free oxide or hydroxide uncombined with other constituents, and reference to the original by those interested for working details of the recommended methods would be essential. The existing literature on the subject, of which a comprehensive bibliography is given, is critically surveyed. From among the varied types of methods which have been tested by the authors, the four following methods have been found to be of value in recent investigations at the Building Research Station: Lerch and Bogue's modification (*Ind. Eng. Chem.*, 1926, **18**, 739; *id., Anal. Ed.*, 1930, **2**, 296) and the Building Research Department's modification of the glycerol extraction method (applicable to unhydrated cements, sand lime bricks and hydraulic lime), the lime-solution extraction method (applicable only to lime mortars and unhydrated lime), and the calorimetric method (devised for hydraulic cements and applicable to mortars and concretes). These methods, together with three methods for the qualitative detection of free lime, are described in detail, and the probable sources of errors and the accuracy obtainable are discussed.

S. G. C.

* Special Report No. 17, by B. Bakewell and G. E. Bessey. H.M. Stationery Office, 1931, pp. 21. Price 6d. net.

Ceylon

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1931

THE Government Analyst (Mr. C. T. Symons) reports that of the 2459 articles examined during the year, 1100 were in connection with 521 criminal cases. Milk adulteration was still high; of 458 samples, 262 were adulterated.

EXAMINATION OF STAINS.—Stained articles were examined in connection with 520 cases. Comment is made upon certain cases in which failure to take elementary

precautions tended to nullify any evidence which might have been available from the scientific examination. In one instance an examination of the deposit under the finger nails for blood, etc., was required, but the prisoner had been at large for 3 days after the crime had been committed, and was then kept in custody for 5 days before being submitted for examination. In another case an exhibit, described as a "mound of earth," and said to be bloodstained, was submitted, but the "mound" had crumbled, and the analyst was expected to find bloodstains in about 20 lbs. of powdery earth.

POISONING CASES.—Poison was identified in 34 of 89 cases. Of these, 9 involved a mydriatic alkaloid (from datura, etc.), 5 arsenic (in one case with zinc chloride), 4 prussic acid, 2 each powdered glass, copper sulphate, hydrochloric acid, acetic acid, and formic acid, and one each morphine, kerosene oil, camphor, and mercury.

Powdered Glass.—Powdered glass may not be considered to be an active poison, but in one case its ingestion with rice caused considerable vomiting in two persons. In the second case a man persuaded another man's wife to introduce the powdered glass into her husband's tea, stating that it would make him of "the same way of thinking as herself."

Formic Acid as a Poison.—The appearance of formic acid in the list of poisons, in addition to acetic acid, was to be expected after its introduction as a rubber coagulant. But the use of such a strong acid in a murder case is unusual. The effects on the stomach walls were similar to those seen with acetic acid.

Prussic Acid.—In a case of prussic acid poisoning, this poison was found in the stomach, but not in the liver, kidneys, and lungs.

FIREARMS AND PROJECTILES.—Forty exhibits were examined in connection with 8 cases. In one case it was found possible to discover traces of lead in a hole in the woodwork of a chair which was said to have been caused by a bullet.

In another case 17 lead pellets and slugs were examined by spectroscopic analysis, and were found to consist of five different types of lead. The same five types of lead found in these pellets from the scene of the crime were all represented in the pellets, etc., found later with the weapon which was suspected to have been used.

The danger of drawing any definite conclusions as to the time which has elapsed since a gun was last fired was again emphasised by the results of examination of guns carried out during the year.

EXAMINATION OF DUST.—In a case of burglary, a breach was made in the wall of a house. The dust from the breach was examined and found to contain minute particles of wood such as occur where a beam of wood is affected with dry rot. Dust extracted from the garments of the suspected burglar was found to contain similar earth dust and wood particles.

SPECTROSCOPIC IDENTIFICATION OF WIRE.—The spectroscope was again instrumental in furnishing trustworthy and rapid evidence of the identity of stolen wire with Government samples.

LECTURES TO THE POLICE.—Two series of lectures were given in 1931, their object being to demonstrate to the police the possibilities arising from the scientific examination of exhibits in cases which depend largely upon circumstantial evidence. It is also hoped that they will have a beneficial effect upon the manner in which products are sent in for examination. It is a matter for regret that an increasing number of exhibits are being sent in from the courts improperly packed and labelled.

Misdescription of Articles as Spirits or Beer

FINANCE ACT, 1932

THE following notice (No. 222) has been issued by the Commissioners of Customs and Excise:—

PENALTIES UPON MISDESCRIBING ARTICLES AS SPIRITS OR BEER

I.—MISDESCRIPTION OF FORTIFIED WINES AS SPIRITS

1. *Misdescription an offence.*—Section 11 of the Finance Act, 1932, prohibits the description of any liquor in any label, wrapper, bill or advertisement of any kind, by any name or words calculated to indicate that the liquor is spirits, or a substitute for spirits, or resembles spirits, or is wine fortified or mixed with spirits, unless spirit duty has been paid on at least 97½ per cent. of the liquor.

2. *Names which amount to misdescriptions.*—A mere name amounts to a misdescription, even though in itself it may not suggest spirits, if it has in the past been used in association with any kind of statement contrary to paragraph 1. The same applies to a name similar to a name which has been so used.

3. *Sale of misdescribed liquors an offence.*—It is likewise an offence to sell or have in possession for sale any liquor misdescribed in the manner explained in paragraph 1 or paragraph 2, whether the misdescription is issued by the seller himself or by some other person.

4. *The effect.*—The effect is that it is illegal to label, advertise, sell or have in stock any liquor, which has not paid duty as spirits, under such names as "brandy wine." The same applies to fancy names which in any way suggest spirits or an admixture of spirits, and to names which are misdescriptions by association, as explained in paragraph 2. All such statements as that a liquor contains spirits, or has the flavour of or in any way resembles spirits, or is wine fortified, mixed or blended with spirits, are equally prohibited. (But see paragraph 11 as to the period of grace.)

5. *Genuine wines and cocktails.*—It is still permissible to use—(i) the recognised names of genuine wines, such as "port" or "sherry," or

(ii) cocktail names which were in use before 4th May, 1932, to describe ready-made brands of cocktails containing vermouth and spirits, the quantity of vermouth in which was at least equal to that of proof spirits.

This only applies to names, and neither wines nor cocktails may be labelled or advertised as fortified or mixed with spirits.

II.—MISDESCRIPTION OF SUBSTANCES AS BEER

6. *Misdescription an offence.*—Section 12 of the Finance Act, 1932, prohibits the description of *any substance* (*i.e.* not merely a liquor, but also, *e.g.* brewing materials in packets), in any label, wrapper, bill or advertisement of any kind, by any name or words calculated to indicate that the substance is, or is a substitute for, or resembles, *ale, beer, porter* or *stout,* unless beer duty has been paid on the whole of the substance.

7. It will therefore be illegal in future to describe liquor below the limits of 1016° in gravity and 2 per cent. in proof spirit content (unless made on licensed brewery premises and duty-paid) by any such names as "bitter ale," "herb beer," or "brown stout," or by any names including the words "ale," "beer," etc. Any words suggesting that a liquor or other substance is, or is intended for use in making, "ale," "beer," etc., will similarly be illegal. (See paragraph 11 as to the period of grace.)

8. The names "ginger beer" and "ginger ale," however, are still permissible.

9. *Sale of misdescribed substances an offence.*—It is likewise an offence to sell or have in possession for sale any substance misdescribed in the manner explained in paragraphs 6 and 7, whether the misdescription is issued by the seller himself or some other person.

III.—PENALTIES

10. The penalty for offences is a fine not exceeding £100, and forfeiture of the offending articles.

IV.—PERIOD OF GRACE

11. In both cases I and II above, up to 30*th September* next inclusive is allowed as a period of grace during which goods may be sold off under the labels, wrappers, etc., under or in which they have been previously sold. This is strictly limited, however, to *labels, wrappers, cartons,* etc., *which go with the goods as sold to the public.* All window-cards, handbills and other advertisements of every kind, if contrary to the law as explained above, must be withdrawn at once.

CUSTOM HOUSE, LONDON, E.C.3
June, 1932

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis

Preservation of Milk for Determination of the Freezing-Point. Rüdiger. (*Chem. Ztg.*, 1932, **56**, 533.)—Neither potassium dichromate nor paraformaldehyde (0·07 per cent.) is recommended, as the results require a correction-factor which is not constant; β-naphthol (0·5 per cent.) is too weak in its effect. Formaldehyde (0·5 c.c. of a 5 per cent. solution in 300 c.c. of milk), mustard oil (0·1 per cent.), or mercuric chloride (0·01 per cent.) may, however, be used to preserve milk for 3 days at 25° C., the temperature-errors being 0·0055°, 0·004° and 0·002° C., respectively; the ordinary experimental error of the method is 0·003° to 0·004° C.

J. G.

Degree of Pigmentation and its Probable Relationship to the Mineral Constituents of Honey. H. A. Schuette and K. Remy. (*J. Amer. Chem. Soc.*, 1932, **54**, 2909–2913.)—Examination of a number of samples of light and of dark floral honeys shows that the former are appreciably poorer in mineral constituents than the latter. The results obtained were as follows:

		Ash	Silica	Iron	Copper	Manganese
		Per Cent.	Mgrms. per kilo			
Light	Minimum	0·04	7·20	1·20	0·14	0·17
	Average	0·06	8·90	2·40	0·29	0·30
	Maximum	0·16	11·70	4·80	0·70	0·44
Dark	Minimum	0·07	5·40	0·70	0·35	0·52
	Average	0·17	14·00	9·40	0·56	4·09
	Maximum	0·52	28·30	33·50	1·04	9·53

It is suggested that the characteristics and flavour of honey are influenced to a marked degree by the nectar and pollen, and that the honey may vary in composition and quality with the meteorological conditions to which the plants are exposed, and with the nature and fertility of the soil. The light honeys include those from alfalfa and clover, and the dark ones those from Spanish needle, tulip poplar, mint, and buckwheat. The methods of analysis are described.

T. H. P.

Accidental Presence of Acrolein in Cider-Brandy. G. Warcollier and A. Le Moal. (*Ann. Falsific.*, 1932, **25**, 271–273.)—In connection with the occurrence of acrolein in the distillates from cider and perry prepared from the last harvest, the following reactions have been investigated:—*Codeine* gave a very fugitive green colour in the presence of sulphuric acid. *Voisenet's reaction* (*Compt. rend.*, 1910, **150**, 879):—A solution of albumin in nitrous hydrochloric acid (composition not given) gave a green colour with 0·1 to 1 mgrm. per litre, and a yellow colour with larger amounts of acrolein; fairly large quantities of acetaldehyde inhibit the reaction, but traces of formaldehyde are without effect. *The Arnold–Mentzel reagent* (phenylhydrazine-hydrochloride and ferric chloride),

which gives a red colour with formaldehyde, turns green in the presence of more than 1 mgrm. of acrolein. With smaller quantities a fugitive red colour, changing slowly to green, is obtained, and if the ferric chloride is omitted the reagent is more specific for acrolein, the intensity of the green colour, which develops in 12 to 24 hours, being proportional to the amount of acrolein present. If 4 c.c. of *Schiff's reagent* (a 0·025 per cent. aqueous solution of magenta decolorised with sulphur dioxide) is added to a cold mixture of about 2 mgrms. of acrolein (in 5 c.c. of solution), and 5 c.c. of 50 per cent. sulphuric acid, a stable apple-green colour develops slowly which is unaffected by small quantities of formaldehyde or acetaldehyde, and which may be matched against that produced from a standard 0·1 to 1·0 per cent. solution of acrolein in 95 per cent. alcohol. In this way 0·050 to 0·100 and 0·120 grm. per litre were found in cider and perry, respectively, and 0·120 to 1·66 and 0·625 in their respective distillates. The acrolein appears to be derived from the glycerin, and it is observed that this conversion may be brought about by micro-organisms, such as *B. amaracrylus* or *B. Welchii*, which may occur in water. J. G.

Unsaponifiable Matter of Coffee-Bean Oil. Preparation and Properties of Kahweol. R. O. Bengis and R. J. Anderson. (*J. Biol. Chem.*, 1932, **97**, 99–113.)—The first part of an investigation of the chemistry of the coffee bean is concerned with the nature and composition of the ether-soluble or fat constituents of the coffee-bean. The unsaponifiable matter represented 10 per cent. of the fat, and was a dark brown semi-solid. It is shown that the unsaponifiable fraction of the fat, extracted from freshly-roasted coffee, contains a large amount of a highly unsaturated, strongly optically active, and sensitive product, which the authors name *kahweol*, together with one or more sterols. The composition of kahweol corresponds approximately with the formula $C_{19}H_{26}O_3$. The substance apparently contains one hydroxyl group, and it melts at 143–143·5° C.; $[\alpha]_D^{21} = -204{\cdot}5°$. Catalytic reduction of kahweol yields a compound having the composition $C_{19}H_{32}O_3$, in which two hydroxyl groups are present. Reduced kahweol melts at 175° C.; $[\alpha]_D^{23} = -67{\cdot}81°$. Kahweol crystallises readily from concentrated solutions, but the form of the crystals varies with the solvent. It is very unstable; pure colourless crystals in a sealed tube filled with carbon dioxide change to a deep yellow colour in less than 24 hours. It would seem that a substance which is so sensitive, as is kahweol, to reagents, light, heat and oxygen, must possess some active physiological properties, but, so far, all tests made have given entirely negative results. A small amount of a phytosterol which was very similar to sitosterol was also isolated from the unsaponifiable fraction of the fat. Its ultimate composition corresponded with the formula $C_{27}H_{45}OH.H_2O$; it melted at 138–139° C., and had optical rotation −35·58°. P. H. P.

Colour Reactions of Novocaine (Procaine), Anaesthesine and Allied Compounds which Distinguish them from Cocaine and Similar Substances. M. Wagenaar. (*Pharm. Weekblad*, 1932, **69**, 727–737.)—The results are summarised below, and an attempt is made to correlate the reactions of these compounds towards various reagents with their structural formulae. Column (1) is Chalmot's reaction (*Amer. Chem. J.*, 1893, **15**, 276), a positive result being a violet colour on

the addition of a crystal of the sample to a drop of furfuraldehyde. Column (3) is the ordinary diazo-reaction (which responds only to NH_2-groups), a positive result being indicated by a red condensation product with a dilute solution of β-naphthol in ammonia or sodium hydroxide solution. Columns (2) and (4) give the results obtained by reactions (1) and (2), respectively, after nitration and reduction, the latter (column 4) being Guerbet's reaction (ANALYST, 1920, **45**, 334; 1921, **46**, 11). The sample is evaporated with a drop of fuming nitric acid, and the nitro-compound is then reduced by the action of a few drops of a dilute solution of stannous chloride. A positive reaction is characteristic of the phenyl group. (See also Gerhardt, *Pharm. Weekblad*, 1926, **63**, 560; and Merz, *Arch. Pharm.*, 1932, **270**, 97, 125.)

Compound	1	2	3	4
Aniline	+	Not tested	+	Not tested
p-Amino benzoic acid	+	,,	+	,,
Anaesthesine	+	,,	+	,,
Novocaine (procaine)	+	,,	+	,,
Tutocaine	+	,,	+	,,
Butyne	+	,,	+	,,
Orthoform	+	,,	+	,,
Pantocaine	—	,,	—	,,
Holocaine	—	,,	—	,,
Diocaine	—	,,	—	,,
Cocaine	—	Pale yellow	—	Pale yellow
β-Eucaine	—	Yellow	—	Yellow
Stovaine	—	Pale yellow	—	Pale yellow
Alypine	—	,,	—	,,

J. G.

Determination of Santonin by means of 2:4-Dinitrophenyl-hydrazine. O. Fernandez and L. Socias. (*J. Pharm. Chim.*, 1932, **124**, 49–54.)—To determine the santonin in wormseed, 10 grms. of the powder are lixiviated with benzene for 24 hours, and, after evaporation of the extract to dryness, 50 c.c. of 15 per cent. alcohol are added to the residue. After being heated for 15 minutes beneath a reflux condenser the liquid is filtered hot, and the flask and paper are washed three times with 5 c.c. of boiling 15 per cent. alcohol. To prevent crystallisation, 85 c.c. of a solution containing 1 grm. of hydrazine in 38 c.c. of water, 38 c.c. of 95 per cent. alcohol and 10 c.c. of sulphuric acid are added. From this point onwards the method is the same as for pure santonin; the hydrazone is formed by the addition of twice the volume of a solution prepared by dissolving 1 grm. of 2:4 dinitrophenyl-hydrazine in 90 c.c. of water to which 10 c.c. of concentrated sulphuric acid have been added, and boiling and filtering, if necessary. After 48 hours' contact in a cool dark place the liquid is filtered, the precipitate is washed with a mixture of 100 c.c. of water and 50 c.c. of 95 per cent. alcohol, dried and weighed. In the case of chocolate containing santonin the fat is removed, the residue is boiled with 95 per cent. alcohol, and, after being filtered, the solution is concentrated and treated as for wormseed with aqueous hydrazine solution, alcohol, and sulphuric acid, and the determination is carried out as for pure santonin. The amounts recovered in nine experiments with pure santonin varied from 98·72 to 99·88 per cent. D. G. H.

Detection of Antipyrine in Pyramidone. P. Duquénois. (*J. Pharm. Chim.*, 1932, **124**, 28–31.)—A modification of the Belgian Pharmacopoeia method is recommended for the rapid detection of antipyrine in pyramidone. When a few c.c. of nitric acid containing nitrous oxides are introduced below the pyramidone solution, a violet ring characteristic of pyramidone is immediately formed, whilst the acid below should be of a yellow-green colour. In the presence of antipyrine a brownish-yellow zone is formed under the violet ring, and in a short time (up to 5 minutes according to the proportion present) with a minimum of 2 per cent. of antipyrine, a green ring of nitroso-antipyrine is formed between the brown and violet zones. D. G. H.

Reduction of Molybdic Reagents by Cherry Laurel Water. F. Morvillez and Defossez. (*J. Pharm. Chim.*, 1932, **124**, 27.)—The positive Pecker's reaction (formation of a blue colour on addition of a solution of ammonium molybdate acidified with sulphuric acid) given by commercial cherry laurel water was found to be due to the constant presence of copper, the presence of tin being only accidental. D. G. H.

Biochemical

Determination of Zinc in Biological Materials. W. R. Todd and C. A. Elvehjem. (*J. Biol. Chem.*, 1932, **96**, 609–618.)—The new micro-method described, which is adapted to amounts of zinc varying from 0·1 to 2·0 mgrms., is based on the precipitation of zinc as zinc ammonium phosphate and a colorimetric determination of the phosphorus in the precipitate (by the Fiske–Subbarow method, ANALYST, 1926, **51**, 205), from which the amount of zinc is calculated. A modification of Fairhall and Richardson's method (*J. Amer. Chem. Soc.*, 1930, **52**, 938), which involves the co-precipitation of zinc with added copper as sulphides, is employed for the preliminary separation of the zinc. *Method.*—The sample is ashed. The ash is dissolved in dilute hydrochloric acid, the filtered solution is diluted to about 30 c.c., and 5 c.c. of sodium citrate solution (100 grms. of sodium citrate dissolved in 300 c.c. of water) and 2 mgrms. of copper as sulphate are added. The solution is adjusted to p_H 3·5 by adding saturated potassium hydroxide solution (brom-phenol blue as indicator), and heated to boiling, and hydrogen sulphide is passed through it until it is cool. The contents of the precipitation flask are transferred to a 50-c.c. Pyrex centrifuge tube (the flask being rinsed out with 10 c.c. of hydrogen sulphide water buffered with sodium citrate and adjusted to p_H 3·5) and centrifuged at 1500 R.P.M. for 5 minutes; the clear liquid is decanted and rejected. The precipitate of mixed zinc and copper sulphides is washed twice by centrifuging with 15-c.c. portions of the special washing solution, described above, and decanting. The precipitate is dissolved by heating it with a mixture of 3 c.c. of water and 0·5 c.c. of concentrated hydrochloric acid, 0·5 c.c. of hydrogen peroxide (30 per cent.) being added, drop by drop, to oxidise the sulphide. The solution is transferred to the original precipitation flask, evaporated to a small volume to destroy the hydrogen peroxide, and diluted to 30 c.c., the zinc and copper are re-precipitated with hydrogen sulphide at p_H 3·5, and the precipitate is dissolved as before. The solution is evaporated almost to

dryness, 22 c.c. of water and 2·5 c.c. of concentrated hydrochloric acid are added, and hydrogen sulphide is passed for 5 minutes to precipitate the copper sulphide, which is separated and washed by the centrifuge method used above, dilute hydrochloric acid saturated with hydrogen sulphide being used for the washing. The solution and washings containing the zinc are evaporated nearly to dryness, and the residue is transferred to a 15 c.c. graduated centrifuge tube; the total volume should be less than 5 c.c. The p_H value is adjusted to 6·6 (brom-thymol blue as indicator), the liquid is heated to 90° C., and 0·5 c.c. of diammonium hydrogen phosphate solution (10 per cent., adjusted to p_H 8–9) is added, drop by drop. The liquid is kept for 30 minutes at 90° C. to enable the initially-formed amorphous precipitate of zinc ammonium phosphate to become crystalline, set aside for 4 hours, and then centrifuged for 5 minutes. The precipitate is washed, by centrifuging and decanting, with 5 c.c. of diammonium hydrogen phosphate solution (1 per cent., rendered faintly pink to phenolphthalein with ammonia), and then with 10 c.c. of alcohol (50 per cent.), the tube being finally left in an inverted position to drain. The precipitate is dissolved in 8 c.c. of 2 *N* sulphuric acid, and the solution is treated with 5 c.c. of a 2·5 per cent. solution of ammonium molybdate in 3 *N* sulphuric acid, and with 2 c.c. of aminonaphtholsulphonic acid solution (0·5 grm. of 1:2:4-aminonaphtholsulphonic acid dissolved in a mixture of 500 c.c. of 5 per cent. sodium bisulphite solution with 5 c.c. of 20 per cent. sodium sulphite solution). After dilution to 50 c.c. the colour developed is compared in a colorimeter with a standard prepared from 2 c.c. of a standard phosphate solution (1 c.c. = 0·1 mgrm. of phosphorus) in a similar manner, except that 5 c.c. of a 2·5 per cent. solution of ammonium molybdate in 5 *N* sulphuric acid are used. The zinc content is calculated from the amount of phosphorus found according to the ratio of zinc:phosphorus in $ZnNH_4PO_4$. Results are cited of test determinations of zinc in pure solutions and in a wide variety of biological materials. S. G. C.

Separation of Vitamin *A*, Carotene and Xanthophyllen. P. Karrer and K. Schopp. (*Helv. Chim. Acta*, **1932**, **15**, 745–746.)—Vitamin *A*, pro-vitamin *A*, and carotene, which often occur together in products of animal origin, like butter and egg-yolk, may be readily separated by chromatographic analysis with the help of adsorbent clay (*Fasertonerde*). A solution of the vitamin *A* and carotene in petroleum spirit is drawn down by suction through a tube filled with the clay, which is afterwards rinsed with a large quantity of petroleum spirit. The upper adsorption layers contain only vitamin *A*, and the lower ones mainly carotene, which may be completely freed from traces of the vitamin by a second adsorption. Elution of the adsorbed compounds is effected as usual with a mixture of petroleum spirit with 10 per cent. of methyl alcohol. Spectroscopic examination of the two carotinoids obtained furnishes evidence of the completeness of the separation.

For separating vitamin *A* from xanthophyll and zea-xanthine, the demixing method is inapplicable, since, in the distribution between petroleum spirit and methyl alcohol, the vitamin and the two oxygenated carotinoids pass into the alcoholic phase. Here, again, chromatographic analysis is effective. If a petroleum spirit or petroleum spirit and benzene solution of the products is filtered through a layer of precipitated calcium carbonate, the vitamin *A* passes

quantitatively into the filtrate, whilst the xanthophyll and zea-xanthine are adsorbed. Doubtless the oxygen-rich carotinoids, viola-xanthine, capsanthin, and fucoxanthine would be similarly adsorbed. T. H. P.

Isolation and Identification of Vitamin *C*. W. A. Waugh and C. G. King. (*J. Biol. Chem.*, **1932**, **97**, 325-331.)—Work on the chemical nature of vitamin *C* has been continued, particularly by the study of the solubility of the active material in organic solvents, leading towards its isolation by crystallisation. The authors describe (*a*) the precipitation of the active material as the lead salt, and (*b*) the isolation of a crystalline compound which is active in the prevention of scurvy in guinea-pigs. The compound (the vitamin) can be recrystallised readily from butyl alcohol, acetone, ethyl acetate, ethyl alcohol, or methyl alcohol, by the addition of petroleum spirit; the appearance of the crystals varies with different solvents. The properties of this active crystalline substance correspond with those given for the "hexuronic acid" studied by Szent-Györgyi (*Biochem. J.*, 1928, **22**, 1387; *J. Biol. Chem.*, 1931, **90**, 385) as an oxidation-reduction factor in adrenal cortex, oranges and cabbage. The two substances are believed to be identical, as previously stated by King and Waugh (*Science*, **1932**, **75**, **357**). The evidence from which the authors conclude that vitamin *C*, as isolated in their laboratory, is identical with the hexuronic acid studied by Szent-Györgyi and Kendall as a reducing factor in plant and animal tissues, is as follows (*i.e.* they correspond in): (*a*) natural occurrence so far as studied (the protective level of 0·5 mgrm. daily of the newly-described preparation corresponds with 0·5 mgrm. of hexuronic acid found by Szent-Györgyi in 1928 in 2 c.c. of orange juice); (*b*) oxidation by iodine and by Benedict's reagent (quantitative); (*c*) specific rotation ($[\alpha]_D^{20} = +25° \pm 1°$); (*d*) acid titration equivalent (exact for the free acid); (*e*) carbon and hydrogen combustion, for $C_6H_8O_6$; (*f*) reversible formation of a lactone and a free acid; (*g*) typical crystal forms; (*h*) solubility in a number of organic solvents; (*i*) precipitation as a lead salt; (*j*) instability toward alkalis and oxidising agents; (*k*) diffusion rate and electrical transference [McKinnis and King (*J. Biol. Chem.*, 1930, **87**, 615; ANALYST, 1930, **55**, 592)]; and (*l*) melting-point (183–185° C.). Further investigations of the two compounds are in progress. P. H. P.

Adventitious Presence of Selenium in certain Plants. Taboury. (*Compt. rend.*, 1932, **195**, 171).—It was shown earlier (*Bull. Soc. Chim.*, 1909, iv, **5**, 865) that the mineral waters of La Roche-Posay (Vienne) contain selenium in appreciable proportions. It is now found that, of the plants growing either in the discharge channel of these waters or on the wet banks of this channel, *Sium latifolium*, L. and *Pastinaca sativa*, L. contain selenium, which could not, however, be detected in *Scrofularia aquatica*, L. The procedure adopted was as follows: The air-dried plant was incinerated at the lowest sufficient temperature, in order to avoid both fusion of the ash and attack of the porcelain dishes used. The ash was treated with water and the clear solution was evaporated to dryness. The residue thus obtained was treated with 35 per cent. alcohol; the evaporated residue from this alcoholic solution was then evaporated with 5 c.c. of hydrochloric acid. Before the whole of the acid had been expelled, the mass was extracted with two quantities

of water (4 c.c. in all), and the liquid treated at 100° C. with 1 c.c. of sodium bisulphite solution. After a few moments any selenium was deposited as a red precipitate. T. H. P.

Organic Analysis

Reactions and Reagents for the Detection of Organic Compounds. I. E. Eegriwe. (*Z. anal. Chem.*, **1932**, **89**, 121–125.)—When a small quantity of a calcium salt precipitate to be tested for tartaric acid is heated to 120° to 150° C. with a few c.c. of a solution of 0·01 grm. of gallic acid in 100 c.c. of 96 per cent. sulphuric acid, a bright blue coloration is obtained in presence of 0·1 to 1 mgrm. of tartaric acid. With diminishing amounts of the acid, the colour changes through bluish-green to yellowish-green (0·002 mgrm.). As little as 0·001 mgrm. of tartaric acid gives a yellowish-green colour if the reagent is prepared by dissolving 0·002 grm. of gallic acid in 100 c.c. of 96 per cent. sulphuric acid. The test may be applied in presence of oxalate or fluoride, but complex iron cyanides must be absent. It yields negative results with oxalic, citric, malic, succinic, formic, acetic, propionic, butyric, lactic, cinnamic, and salicylic acids, but positive results are obtained with glycollic, tartronic, glyceric, and glyoxylic acids, formaldehyde or carbohydrates.

Malic acid gives a bluish fluorescence when heated in a water-bath with a reagent made by dissolving 0·0025 grm. of β-naphthol in 100 c.c. of 96 per cent. sulphuric acid; when 1·5 c.c. of the reagent is used, 0·01 mgrm. of malic acid is detectable. Malic acid may be identified in this way in presence of citric and succinic acids, the test being made on the calcium salt precipitate or, if this is small in quantity, on a drop of its solution in dilute sulphuric acid. The reaction is not given by oxalic, tartaric, citric, succinic, cinnamic, benzoic, salicylic, acetic, or formic acid, but certain hydroxy-acids of the glycollic series give a marked or a faint (acids of the tartaric series) green fluorescence. Glycollic acid, which may occur in the calcium precipitate, gives a brownish-yellow coloration which masks the fluorescence due to the malic acid.

When heated for 15 to 25 minutes in a water-bath with 10 c.c. of a solution of 0·01 grm. of 2:7-dihydroxynaphthalene in 100 c.c. of concentrated sulphuric acid, 1 mgrm. of glycollic acid gives a deep red coloration with a violet tinge; with 2 c.c. of the reagent, 0·0002 mgrm. of the acid yields a bright pink colour. Solutions containing over 1 mgrm. of glycollic acid per drop (0·05 c.c.) must be diluted before being tested. Formic, acetic, oxalic, succinic, citric, benzoic, and salicylic acids give no coloration with this reagent, but lactic and malic acids yield a yellow solution with green fluorescence, and tartaric acid gives an olive-green or dark greenish-brown colour. Certain oxidising agents, such as persulphates, hydrogen peroxide, chlorates and chromates, gradually give a violet colour to the reagent, which by itself assumes a faint red or reddish-violet colour if left exposed to the air for some hours.

Since oxalic acid is readily reduced to glycollic acid by means of powdered magnesium and dilute sulphuric acid, it may be detected, after reduction, by the 2:7-dihydroxynaphthalene reagent. Glyoxylic acid also gives glycollic acid on reduction, and hence gives the same colour reaction as oxalic acid; it is, however, not precipitated from neutral solution by calcium sulphate solution. T. H. P.

Detection of Oxygen in Liquid Organic Compounds. T. Estreicher. (*Z. anal. Chem.*, 1932, **89**, 126–128.)—According to Wüstner (*ibid.*, 1932, **87**, 114), a liquid organic compound which dissolves iodine forms brown solutions of this halogen if it contains oxygen, or violet solutions if it is oxygen-free. It is found, however, that, for 28 per cent. of the whole number of such solvents, this rule is not obeyed. T. H. P.

Determination of Small Amounts of Ethyl Iodide. R. D. Cool. (*J. Biol. Chem.*, 1932, **97**, 47–52.)—The use of ethyl iodide in the indirect determination of cardiac output in man gives importance to methods for the determination of its vapour in air and water. For this purpose an iodate method is described in which chlorine or bromine is used to oxidise the iodide to iodate; the excess halogen is removed with phenol, and iodine is liberated from potassium iodide by the iodate, and determined by titration with thiosulphate. The procedure applicable to air samples containing vaporised ethyl iodide is as follows: The mixtures of ethyl iodide and air are collected in the 500-c.c. gas-sampling tubes previously described; 10 c.c. of chlorine water (containing approximately 0·35 per cent. of chlorine) not more than a day old, are placed in a reagent tube which is inserted into the end of one of the rubber connections on the sampling tube so that the pinch-clamp can be removed without allowing gas to escape. The reagent tubes are made of glass tubing slightly narrower than the neck of the sampling tube, with a 10-c.c. bulb blown at one end. The pinch-clamp is removed, the mouth of the reagent tube is pushed through the rubber tubing until it is 2 to 3 cm. within the glass neck of the sampling tube, and the chlorine water is allowed to run into the main body of the sampling tube, but not into the opposite neck; the walls are washed with the reagent by rotation of the tube. The contents of the reagent and sampling tubes are washed into an Erlenmeyer flask with a total of 30 to 35 c.c. of distilled water divided into at least three portions. The liquid in the flask is rotated, and 10 c.c. of 10 per cent. phenol-water mixture are added *rapidly* from a graduated cylinder. After the solution has stood for at least 20 minutes, 25 c.c. of water and 5 c.c. of 20 per cent. potassium iodide solution (prepared on the day it is to be used) are added, and the iodine liberated is titrated, at once, with 0·005 *N* sodium thiosulphate. When the yellow colour of the iodine has nearly disappeared, 5 c.c. of 0·2 per cent. starch solution are added, and the titration is continued until the solution is colourless. One c.c. of 0·005 *N* sodium thiosulphate is equivalent to 0·130 mgrm. of ethyl iodide in the original sample. When the highest analytical accuracy is required the 0·005 *N* sodium thiosulphate solution must be made with recently boiled distilled water, must not be more than 2 weeks old, and must be standardised each day. Five c.c. of approximately saturated bromine water (containing about 2·5 per cent. of bromine) may be used, instead of the 10 c.c. of chlorine water, in the above procedure, and the excess removed with 5 c.c. of aqueous 10 per cent. phenol solution. Experiments carried out to test the accuracy of the method are described. In the range of quantities of ethyl iodide dealt with in an indirect determination of cardiac output the average error was 0·011 mgrm., or 0·5 per cent. This is approximately one-third the error found by Starr and Gamble (*J. Biol. Chem.*, 1927, **71**, 509; ANALYST, 1927, **52**, 168) in their silver

nitrate method, and may be held responsible for an error of only 2 to 3 per cent. in the value for cardiac output. The method described is at once directly applicable as an improvement in the analytical technique of the Starr and Gamble cardiac output method. P. H. P.

Detection and Determination of Dichloro-Ethyl Sulphide by Combustion. M. Maxim. (*Chem. Ztg.*, 1932, **56**, 503.)—The usual methods for this determination (liberation of iodine from hydriodic acid followed by titration, or reduction of selenic acid to selenium, which is weighed) are not specific. Air is, therefore, drawn in succession through a wash-bottle containing potassium permanganate solution, and then over dry calcium chloride, and, finally, through a wash-bottle containing a solution of the sample in 50 c.c. of pure benzene (free from thiophen). It then passes through a glass combustion-tube maintained at red heat, and filled with broken pumice, except for a layer in the centre, 5 cm. long, which contains platinised asbestos. The emerging vapours are made to bubble through a 20 per cent. solution of barium chloride, to which 20 c.c. of perhydrol have been added, and the resulting barium sulphate is weighed; the error on 1·3 grm. of dichloro-ethyl sulphide is −0·34 to −0·59 grm. Alternatively, the contents of a gas-chamber may be drawn through a meter directly into the combustion tube. J. G.

Dichloro-ethylene as a Solvent. D. Mann. (*Chem. Ztg.*, 1932, **56**, 452.)—Not only is dichloro-ethylene less inflammable than ether, but it is also preferable as an extracting solvent on account of its selectivity for certain *o*-compounds. Thus, at 20° C., 1 grm. of *o*-nitrophenol, dihydroxybenzene and hydroxy-benzoic acid dissolve in 0·9, 97·5 and 137·0 c.c. (±0·5 c.c.), respectively, the figures for the corresponding *p*-compounds (1·0, 0·01 and 0·01 grm., respectively) being 62·5, more than 200, and more than 300 c.c. On shaking a mixture of 2 grms. each of *o*- and *p*-nitrophenols with 20 c.c. of this solvent, 95·3 per cent. of the former (m.pt. 214° C.) was recovered. The method may also be used in conjunction with steam-distillation for the separation of these isomers from the reaction-mixture obtained by the usual method of preparation. J. G.

Colorimetric Method for the Determination of Tartaric Acid. P. F. Underhill, F. I. Peterman and A. G. Krause. (*J. Pharm. Exp. Therapeutics*, 1931, **63**, 351–358.)—The method described was developed for determining small quantities of tartaric acid in connection with studies in the metabolism of tartrates, and has also been applied in the rapid analysis of baking powder, etc. It depends on the fact that, whereas on acidification of a colourless solution of sodium metavanadate with acetic acid a yellow or orange colour is produced, in the presence of tartaric acid the resulting colour is red (*cf.* Mitchell, ANALYST, 1903, **28**, 146). The depth of colour, which reaches a maximum in 10 minutes and thereafter fades, is dependent on the quantity of tartrate present. The reaction is given by racemic acid, but not by mesotartaric acid; none of the other fruit acids interfere. Lactic acid in high concentration yields a red colour, which fades rapidly. Oxalates alone give a rose colour with vanadate, but tests showed that mixtures of oxalate and tartrate give a colour corresponding only with the tartrate present in the mixture. In strong solution certain substances may interfere, but the quantities

necessary for interference are greater than those encountered in excretions or fluids of the body. *General Method.*—To the clear colourless neutral solution to be tested, contained in a 50-c.c. Nessler tube, 1 c.c. of glacial acetic acid and 4 c.c. of sodium metavanadate solution (5 per cent.) are added, and the liquid is diluted to 50 c.c. After ten minutes the colour is compared with a range of standards, prepared at the same time, by treating different amounts of tartaric acid solution (1 mgrm. per c.c.) in the same manner. The standards should contain from nil to 2 mgrms. of tartaric acid in intervals of 0·1 to 0·2 mgrm., depending on the accuracy desired. In the range 1·0 to 2·0 mgrm. of tartaric acid it is stated to be possible, with practice, to distinguish differences of 0·1 mgrm. *Urine.*—The method has been applied to human urine and to that of the dog, rabbit, guinea pig and rat. The urine is decolorised by boiling with vegetable charcoal ("norit"), and the whole or an aliquot part of the filtered liquid, neutralised to phenolphthalein with sodium hydroxide, is used for the tartrate determination. *Faeces.*—About 2 grms. are weighed into a wide-mouthed bottle; 75 c.c. of boiling dilute trichloroacetic acid (2 per cent.) are added, the mixture is stirred until cool, diluted to 100 c.c. with the dilute trichloroacetic acid, 4 grms. of purified "norit" are added, and the mixture is stirred for 30 minutes and filtered through a dry filter paper. The solution is neutralised, and aliquot parts are taken for the tartrate determination. In test experiments tartaric acid and tartrates added to faeces were recovered with an error of 5 per cent. *Blood.*—To 5 c.c. of oxalated blood 25 c.c. of trichloroacetic acid solution (5 per cent.) are added, and the liquid is diluted to 50 c.c. After 15 minutes the liquid is filtered, the filtrate (which should be clear and colourless) is neutralised, and an aliquot part is taken for the determination. The foam which occasionally persists on the liquid in the Nessler glass may be discharged by the addition of 1 drop of ether. *Tartrate Baking Powder.*—One grm. of the baking powder is suspended in 250 c.c. of water, the residual starch is filtered off, and 1 or 2 c.c. of the filtrate is taken for the tartrate determination. The results recorded for the tartaric acid content of four samples of baking powder, obtained by this and by the A.O.A.C. (1925) method, agree fairly well. *Grape Juice.*—A mixture of 5 c.c. of grape juice, 25 c.c. of water, and 2 grms. of purified "norit" is boiled for 4 minutes and filtered, and the residue is washed. The filtrate is neutralised, diluted to 100 c.c., and aliquot parts of 2·5 and 5 c.c. are taken for the tartrate determination. The recorded results of analyses of six commercial samples, obtained by this and by the A.O.A.C. (1925) method, show, in general, good agreement. *Note.*—The purified "norit" used where specified was prepared by boiling 1 part of "norit" with 4 parts of hydrochloric acid (11 per cent.) for 15 minutes, filtering off and drying the residue, and heating it to dull redness for 30 minutes in a closed electric furnace; it is stored in an air-tight container. S. G. C.

Determination of Hemicelluloses by Oxidation with Potassium Dichromate. A. Jäger. (*Chem. Ztg.*, 1932, **56**, 570–571.)—Experiments are described which indicate that the conditions necessary in order to avoid auto-reduction of the potassium dichromate during the heating process are as follows:—To a cool mixture of 10 c.c. of 8 per cent. potassium dichromate solution and 15 c.c.

of concentrated sulphuric acid (or 10 c.c. when dextrose is to be determined) are added about 5 c.c. (x c.c.) of the sample, and the whole is heated at 125° to 135° C. for 5 minutes. The solution is then cooled and, after dilution with 150 to 200 c.c. of water, the excess of potassium dichromate is titrated with 0·1 N ferrous ammonium sulphate solution (y c.c.) with a 2 per cent. solution of potassium ferricyanide as a spotting indicator. Then, from the equation:—

$$\frac{0{\cdot}8 - (y0{\cdot}00491) \times 0{\cdot}1375 \times 1000}{x}$$

the amount of hemicelluloses in grms. per litre is obtained. If it is necessary to work in greater dilution (*e.g.* when using the filtrate from α-cellulose determinations), the solution should be boiled (at 125° to 135° C.) for 10 and 15 minutes when 20 and 50 c.c. of sample, respectively, are taken (*cf.* H. Schmidt, *id.*, 1932, **56**, 273).

J. G.

Colour Reactions of Sterols. E. Montignie. (*Bull. Soc. Chim.*, 1932, **51–52**, 690.)—Evaporation of a dilute alcoholic solution of cholesterol in the presence of a few drops of an alcoholic solution of silico-tungstic acid results in the formation of a red-brown coloration. The phytosterols, stigmasterol and ergosterol give similar reactions, but the α- and β-cholesterylenes and cholestenone give only faint yellow-red colours. Oil of turpentine, cineole, terpenes, camphor and borneol give orange-red colours, and menthol, oil of lemon, abietic acid and other compounds containing several benzene nuclei (such as chrysene, phenanthrene, anthracene and naphthalene) give negative results. The reaction is specific for indene, small traces of which give a carmine-red colour. D. G. H.

Colour Reaction of Pyrrolic and Indolic Compounds. E. Montignie. (*Bull. Soc. Chim.*, 1932, **51–52**, 689–690.)—*Pyrrol.*—Eight to 10 drops of a 10 per cent. solution of selenious acid and 1 c.c. of concentrated nitric acid boiled with an aqueous solution of pyrrole yield a dark violet colour. The reaction is sensitive to 0·00004 grm. of pyrrole. *Indol* also yields a violet colour, and by this means 0·00005 grm. may be detected. With *scatoll*, on the other hand, a red colour results, but without nitric acid the colour is violet, turning to red on addition of the acid. With *tryptophan*, a citron-yellow colour is formed on heating, with or without the addition of nitric acid to the aqueous solution. D. G. H.

Detection and Estimation of Chemical Damage in Wool. P. Krais. (*J. Text. Inst.*, 1932, **23**, 144–146.)—The author maintains that damage in wool should not be assessed only on colour or chemical reactions. Corroboration by mechanical tests is essential, since it is mechanical strength and elasticity which count in practice. Furthermore, certain chemical damages may show in the amount of soluble nitrogen, but have no effect on the mechanical properties. The test for soluble nitrogen is as follows:—The sample (0·1 grm.) is kept for three days in a mixture of 8 c.c. of water, 10 c.c. of 1 per cent. hydrogen peroxide, and 2 c.c. of 0·5 N potassium hydroxide solution. The soluble nitrogen is in the form of ammonia, amino-carboxylic acids, etc., and is calculated in per cent. of the total nitrogen. In a fine undamaged wool this figure will be 4 to 5, and may rise to 32 or more in the damaged condition.

A table is given comparing the soluble nitrogen figure with breaking strength and extension for two samples of wool in the original condition; and (*a*) treated for 3 hours at 80° in 3 per cent. sodium carbonate solution; (*b*) bleached with 0·1 per cent. potassium permanganate solution containing excess of sulphuric acid, followed by sodium bisulphite and sulphuric acid; (*c*) boiled for 3 hours under a reflux condenser, with 0·2 per cent. sulphuric acid; (*d*) boiled for 10 hours with 0·5 per cent. sulphuric acid. The treated samples were rinsed and dried at the ordinary temperature.

In the case of one sample of wool, the soluble nitrogen figure was 3·42, and in the treated wools rose to 3·91, 3·77, 3·91, and 9·58, respectively. The breaking strength (dry) was 11·2 in the original sample, and in the treated samples 11·7, 10·3, 11·1, and 6·7. The breaking strength (wet) was 74 per cent. of the corresponding "dry" value, but only 48 per cent. after treatment (*a*). The extension at the breaking point rose from 38 (dry) to 64 per cent. (wet) in the original, and from 34 to 51 per cent. after treatment (*a*), but after treatment (*d*) the percentage extension rose from 3·2 (dry) to 34 (wet). Figures are also given for extension curves (dry and wet) and breaking strength in kilos. The author suggests that the test for soluble nitrogen be abandoned, and that reliance be placed exclusively on mechanical tests. R. F. I.

Inorganic Analysis

Comparison of the Reaction-Capacity towards Oxygen of Different Absorbing Materials used in Technical Gas Analysis. E. (*Chem. Ztg.*, 1932, **56**, 452.)—In order to remove all the oxygen from 100 c.c. of air, six treatments with a solution of 50 grms. of sodium hydrosulphite in 250 c.c. of water and 40 c.c. of 5:7 sodium hydroxide solution were required; five with a similar mixture in which the sodium hydroxide was replaced by 130 c.c. of 1:3 potassium hydroxide solution; five with a solution of chromous acetate in 10 per cent. sulphuric acid; and three with a mixture of equal volumes of saturated pyrogallol and potassium hydroxide solution (1:3). J. G.

Thiosulphate as an Acidimetric Standard. J. Bicskei. (*Z. anal. Chem.*, 1932, **88**, 414–417.)—Chemically pure, powdered sodium thiosulphate (0·2 to 0·5 grm.) is accurately weighed and dissolved in a little water. The solution is treated with 2 c.c. of 4 per cent. potassium iodate solution, 0·3 grm. of potassium iodide and 2 c.c. of starch solution, diluted to 50 to 100 c.c., and titrated to the blue end-point with the acid to be standardised:

$$6HCl + KIO_3 + 5KI + 6Na_2S_2O_3 = 6KCl + 6NaI + 3H_2O + 3Na_2S_4O_6.$$

The above quantities refer to 0·1 *N* acid; for *N* acid, tenfold quantities of thiosulphate, iodate, and iodide are prescribed. W. R. S.

Colorimetric Determination of Small Amounts of Silver. E. E. Jelley. (*J. Soc. Chem. Ind.*, 1932, **51**, 191–193T.)—The method is based on the reduction of an ammoniacal silver solution by sodium hyposulphite (hydrosulphite) in the presence of gelatin to form a clear yellow silver solution. The following solutions are required:—(1) *Standard ammoniacal silver solution* (containing 0·1 mgrm. of

silver per c.c.) prepared by diluting a mixture of 9·25 c.c. of 0·1 *N* silver nitrate solution and 25 c.c. of ammonia (sp.gr. 0·88) to 1 litre with copper-free water, *i.e.* water which gives no yellow coloration with sodium diethyldithiocarbamate reagent (*cf.* ANALYST, 1929, **54**, 652; 1932, 495); this solution keeps well; (2) *Ammoniacal gelatin solution*, prepared by dissolving 2 grms. of "de-ashed" gelatin in water, adding 100 c.c. of ammonia (sp.gr. 0·88), and diluting to 1 litre (if ordinary gelatin is used, 0·2 grm. of ammonium phosphate should be added to precipitate any calcium or magnesium which it may contain). *Method.*—To the strongly-ammoniacal solution containing the silver (up to 1 mgrm.) to be determined, are added 10 c.c. of the ammoniacal gelatin solution and 0·4 grm. of sodium hyposulphite, and the volume is adjusted to 50 c.c. by the addition of approximately *N* ammonia. After thorough mixing, the liquid is warmed to 50° C. The quantity of the standard silver solution required to produce approximately the same depth of colour is treated similarly, and the colorimetric comparison is made with a Kober colorimeter. The colour fades after several hours, but satisfactory results were obtained in test experiments up to one hour after preparation. Copper, cobalt, nickel and cadmium interfere, and must be separated. The method described is to add an excess of bromine water and hydrobromic acid to the solution, which is evaporated until the silver bromide forms a coherent deposit; the precipitate is collected in a sintered glass crucible, washed with water, and the silver bromide dissolved in ammonia for the colorimetric determination. The silver content of silver and silver sulphide sols may be determined by adding bromine water to convert the silver into bromide, followed by a few drops of sodium sulphite, and then rendering the solution ammoniacal; calcium and magnesium, if present, should first be precipitated by the addition of ammonium phosphate. S. G. C.

Solubility of Antimonious and Stannic Sulphides in Ammonia and Ammonium Carbonate. P. A. Epik. (*Z. anal. Chem.*, 1932, **89**, 17–23.)—A familiar procedure for the qualitative separation of arsenic from tin and antimony is based on the differential solubility of the sulphides in ammonia and ammonium carbonate solutions. The author, investigating the solubility of antimonious and of stannic sulphides in these solutions, found that ammonia dissolves considerable quantities of the two sulphides, especially on warming. Antimonious sulphide is practically insoluble in ammonium carbonate solution, whilst stannic sulphide shows a solubility of 0·17 grm. per 100 c.c. of the saturated solution. According to the experimental evidence, the qualitative procedure under discussion is not sound, and its use should be discouraged. W. R. S.

Determination of Carbon Disulphide in Benzene. T. Callan, J. A. R. Henderson and N. Strafford. (*J. Soc. Chem. Ind.*, 1932, **51**, 193–194T.)—The interaction of carbon disulphide, diethylamine and a copper salt yields an intensely brown-coloured product which is employed as the basis of the following colorimetric method. To 1 c.c. of the benzene under test (containing less than 0·0001 grm. of carbon disulphide) contained in a narrow Nessler cylinder, 1 c.c. of diethylamine solution (1 c.c. per cent. in benzene which has been purified by "refluxing" with alcoholic potash, washing with water until free from alkali, and finally distilling),

and 1 c.c. of copper acetate solution (0·03 per cent. in alcohol) are added, and the whole is diluted to 10 c.c. with alcohol. The colour developed is compared with a range of standards prepared by treating 0·25, 0·5, 0·75 and 1 c.c. of a solution of carbon disulphide in purified benzene (1 c.c. = 0·0001 grm. of carbon disulphide) in the same way; the copper acetate and the alcohol should be added to the test solution and the standards at the same time, and the mixtures kept for 20 minutes before making the final comparison. As little as one part of carbon disulphide in 1,000,000 parts of benzene can be detected. Pure thiophen gives no colour in the test. The method can be applied to the determination of carbon disulphide in such liquids as toluene, xylene, carbon tetrachloride, etc. Tests of the method in two independent laboratories gave good results. S. G. C.

Microchemical

Alkalimetric Micro Method for the Determination of Chlorine and Bromine in Organic Material. M. K. Zacherl and H. G. Krainick. (*Mikrochem.*, 1932, **11**, 61–73.)—The substance is oxidised with a mixture of potassium dichromate and silver dichromate in sulphuric acid, the halogens liberated are absorbed in a standard alkaline solution containing hydrogen peroxide (perhydrol), and the resulting halogenides are titrated. *Reagents*: (1) Concentrated sulphuric acid (sp.gr. 1·84); (2) pure potassium dichromate; (3) silver dichromate, prepared by Autenrieth's method (*Ber.*, 1902, **35**, 2057); (4) pure hydrogen peroxide (perhydrol); (5) sodium hydroxide and hydrochloric acid (0·01 *N* solutions), prepared by the Pregl method; (6) sodium methyl red as indicator. *Procedure*: For a substance containing chlorine the optimum weight of material is 4 to 5 mgrms.; for bromine, 5 to 6 mgrms. The substance is weighed in a weighing tube, such as that used by Lieb and Krainick (*Mikrochem.*, 1931, **9**, 367), and transferred to the clean dry oxidation flask, which is similar in shape to a Kjeldahl flask, with a bulb 1·8 cm. in diameter. About 0·5 grm. of a mixture of equal parts of potassium dichromate and silver dichromate is put into the flask. The absorption tube, which has the shape of a burette and is 1·2 cm. in diameter, with a glass tap at the bottom, contains a glass spiral which fits round the glass tube leading from the oxidation flask. Thus a small volume of liquid in the absorption burette has a considerable depth, which facilitates the complete absorption of the halogens in the gas bubbling through it. Into the absorption burette 1 c.c. of perhydrol, and then 7·5 c.c. of 0·01 *N* sodium hydroxide solution from a micro burette are added. A small tap funnel with an external ground-glass joint is attached to the oxidation flask, and the side tube from the oxidation flask is passed to the bottom of the absorption liquid. Then 2 c.c. of concentrated sulphuric acid are placed in the tap funnel, the tap of which is connected with an oxygen cylinder through a washing solution of sodium bicarbonate. The oxygen is turned on, at the rate of 10 bubbles in 6 seconds (about 8 c.c. per minute), and the tap of the tap funnel is opened cautiously. The oxidation flask is lowered into the paraffin or glycerin bath, and heated for 30 minutes at 115° to 125° C., during which time the apparatus requires no attention. The top of the tap funnel is then closed, and the top of the absorption burette is opened so that its contents may run out into a quartz-glass conical flask. The absorption burette is washed three times with 4 c.c. of

distilled water, a drop of methyl red is added, followed by a slight excess of 0·01 *N* hydrochloric acid, and the contents of the flask are boiled to drive off carbon dioxide. If necessary, a further drop of indicator is added, and the solution is titrated, while hot, with 0·01 *N* sodium hydroxide solution. The acidity of 1 c.c. of the perhydrol (which is usually equivalent to 0·06 to 0·16 c.c. of 0·01 *N* alkali) is subtracted from the titration value in a determination; for the calculation 1 c.c. of 0·01 *N* sodium hydroxide is equivalent to 0·3456 mgrm. of chlorine or 0·7992 mgrm. of bromine. The method gives excellent results with biological material, for which it is especially designed, and for a large number of pure compounds, including di-nitro compounds, but has not yet been adapted for very volatile liquid substances. (Complete apparatus from P. Haack, Vienna.) J. W. B.

Microchemical Reactions of Saccharin. M. Wagenaar. (*Pharm. Weekblad*, 1932, **69**, 614–618.)—Saccharin is soluble in alcohol and in 400 parts of cold water or 30 parts of boiling water, and is slightly soluble in ether, chloroform or benzene. It sublimes in small rosettes, and 0·05 mgrm. (1:100) is detectable by precipitation with a mineral acid from a solution in alkali. Silver nitrate gives dark micro-rosettes (0·02 mgrm., 1:200) on addition to a solution of the sodium salt; cadmium sulphate gives isolated prisms (0·025 mgrm., 1:200); pyridine and copper sulphate (Zwikker, ANALYST, 1931, **56**, 758) give well-defined oblong crystals; and mercuric chloride, added to a solution of saccharin in a slight excess of sodium hydroxide solution, gives prismatic crystals (0·01 mgrm., 1:300). Iodine dissolved in potassium iodide solution precipitates dark, weakly-dichroic needles, and 0·01 mgrm. (1:300) is detectable if 1 drop each of hydrochloric acid, hydrogen peroxide and a small crystal of potassium iodide are added in succession to the sample. These reactions were tested on beer and lemonade containing added saccharin, which was extracted in ether and then obtained by evaporation. J. G.

Note on the use of Sand for Centrifuging Small Precipitates. S. Stene. (*Mikrochem.*, 1932, **11**, 131–132.)—Two kinds of sand are used: (1) Purified sea-sand, in which the size of grain is less than 0·5 mm. (2) Merck's quartz-sand, washed and ignited; the grains are mostly long in shape, the greatest length being 2 to 5 mm. In micro-centrifuge tubes (pointed) about 5 grms. of sand are used, and in cylindrical tubes about 5 mm. of sand. The addition facilitates both the settling and the washing of the precipitate, but a little more washing liquid should be used. J. W. B.

Physical Methods

Radioactivity of Musts and Wines. E. Canals and A. Médaille. (*J. Pharm. Chim.*, 1932, **124**, 62–67.)—Nodon and Cuvier (*Compt. rend.*, 1928, **187**, No. 17) have stated that wines are invariably radioactive, such activity, in the case of the white and red wines studied by them, being sometimes equivalent to one-tenth of that of uranium oxide, but varying with the vineyard and the season. The wines of Roussillon had a radioactivity ranging between 0·074 and 0·129 millimicrocuries, *i.e.* much less than that given above. The modification of the

Curie electroscope, as used by Laborde and Chenéveau, was employed, but curves analogous to those given by them could not be obtained. Matured wines were less active than new wines; on the other hand, the latter appear to be more radio-active than the grapes (musts). D. G. H.

Reviews

A TEXT-BOOK OF ORGANIC CHEMISTRY. JULIUS SCHMIDT. Second English Edition. H. GORDON RULE. Pp. xxiv+843. London: Gurney & Jackson. Price 25s. net.

The fact that a new edition of this work should be required within six years of the publication of the first English edition shows that an advanced text-book on organic chemistry was not superfluous in this country. Whilst several shorter text-books might be mentioned, works of the type now under review have not been largely represented; perhaps the much-used Richter–Spielmann is the nearest approach. Cohen's excellent work is written from a different point of view; the new Schmidt-Rule is what it claims to be—a text-book. It is, however, a somewhat advanced text-book, and the user is expected to have a good working knowledge of elementary inorganic, organic and physical chemistry.

The order in which the very extensive subject-matter is arranged follows the usual lines, preliminary matters are disposed of with commendable brevity, and the general treatment is modern in type. There is an Introduction of 97 pages, and this is succeeded by three main divisions, *viz.* Aliphatic or Fatty Compounds (98–346), Carbocyclic Compounds (347–560), and Heterocyclic Compounds (561–793). Strictly speaking, heterocyclic compounds do not occupy the whole of Part III, which contains sections on Proteins (IX, 754–776), Chlorophyll and Other Plant Pigments (X, 776–790), in which some description of Carotinoids and Anthocyanins is given, and Enzymes (790–793). The Author and Subject Indexes which complete the work, are commendably full.

Considerable alterations have been made in the Introduction to this new edition; the early history of Organic Chemistry is dismissed in less than two pages, and the analysis of organic compounds and the determination of their molecular weights are only briefly described. The reviewer thoroughly approves of this procedure, as about eighty pages are thus available for the discussion of general topics before the systematic treatment of different classes of compounds.

In addition to the exposition of structure on classical lines, an account is given of the electronic theory of valency based on the views of G. N. Lewis, Lowry, Sidgwick and Sugden. This is followed by a section on Stereo-Chemistry, in which the earlier work relating to the asymmetric carbon (Le Bel, van't Hoff) and nitrogen (Pope) atoms is dealt with in a condensed manner, and methods of resolution are indicated. The few pages devoted to conditions for enantiomorphism are clear, and opportunity is taken to describe the type of optical isomerism, discovered by Christie and Kenner, which is now explained by the theory of restricted rotation (Bell and Kenyon, Turner and Le Févre, Mills,

Meisenheimer). The questions of asymmetric synthesis (McKenzie, Marckwald, Rosenthaler, Bredig) and asymmetric decomposition (Cotton, S. Mitchell, Kuhn) are then discussed, and under the head of geometrical isomerism the results obtained with compounds containing doubly-linked carbon atoms and ring- or spiro-structure are briefly mentioned. Short accounts follow of the stereo-isomerism attributed to the presence of nitrogen or other atoms. It is hardly necessary to add that stereochemical matters crop up at intervals throughout the descriptive portion of the work; thus the chief reference to the Walden inversion is to be found on p. 278.

A short section of the Introduction (10 pages) is devoted to Tautomerism (Desmotropism, Dynamic Isomerism), and a classification is made of the principal systems exhibiting this phenomenon. The reader who wishes for more concrete examples may find many by use of the Subject Index.

Rather more than twenty pages are given to the physical properties of organic compounds; these are considered in the following order: colour, state of aggregation, melting point, boiling point, solubility, density, the parachor, electrical conductivity, polar properties, optical behaviour and heats of formation and combustion.

In the descriptive portion of the book, the order followed is fairly conventional, but the treatment is distinguished by reference to compounds which have acquired technical importance, or which are now prepared by more convenient methods than those adopted by their discoverers. To take a few examples, reference may be made to the synthesis of petroleum hydrocarbons and methanol, the halogen derivatives of ethane and ethylene, fermentation glycerol, tetralin, decalin, etc. One is somewhat surprised to find no reference to the hydrolysis of trichloroethylene or of dichlorovinyl ethyl ether.

Organic chemistry was originally concerned with the compounds isolated from animals and plants or produced from these substances by chemical reactions. The authors have, as far as possible, treated natural products in those sections of the work where they systematically belong. Thus, directly following on the monobasic fatty acids, there is mention of the phosphatides, whilst dihydric alcohols lead on to bases which stand in a genetic relationship to them, *e.g.* hydroxyethylamine, choline, muscarine, neurine, the polymethylenediamines and taurine. The reviewer was interested to read on page 240 that muscarine possibly has the structure $(HO)_2CH.CH_2.N(CH_3)_3OH$. The production of an optically active dihydroxy-*n*-valeric acid by the Hofmann degradation of the base, recently effected by Kögl, Duisberg and Erxleben, shows that this is not the case. (The reviewer thanks the authors of an ingenious detective novel for calling his attention to the optical activity of muscarine.)*

A section on aldehydic and ketonic alcohols (pp. 286–321) includes an account of the carbohydrates which is somewhat condensed. The reaction of acetone with certain compounds containing the group –CHOH.CHOH– should have been mentioned both here and in connection with the hydroxy-derivatives of cyclohexane. A short account of the cyanogen compounds includes mention of the

* *The Documents in the Case.* By Dorothy L. Sayers and Robert Eustace. London: Ernest Benn Ltd., 1930.

isomerism of cyanuric acid and cyamelide. Among derivatives of carbonic acid, urea and thiourea are described, but the tautomerism of these compounds is treated too briefly. The ureides follow, and ten pages are given to them; this has to include an account of the purine group.

Taking other naturally occurring products in order, we find muscone and civetone mentioned under cyclo-olefines, and the chemistry of rubber is discussed immediately afterwards. Tannins are described in connection with phenolic acids. In the 28 pages allotted to the hydro-aromatic compounds, most space is given to the terpenes and camphors; a short account of the sterols and bile acids is also given. Considering the limited space, the treatment is satisfactory.

In Part III, dealing with heterocyclic compounds, about twenty pages are given to the pyrrole group; in this way it has been possible to give a longer account of the colouring matters of leaves and blood than is usual in text-books. A further nine pages is allotted to chlorophyll at the end of the book.

Alkaloids are defined on page 663 as basic compounds of vegetable origin, in which at least one nitrogen atom forms part of a cyclic system. Over seventy pages following on the sections dealing with pyridine, quinoline and acridine are allotted to their chemistry. Only a brief account is given of the *Strychnos* alkaloids, the reader being referred to the original literature. About forty pages at the end of the book are occupied with proteins, plant pigments (including carotinoids and anthocyanins) and enzymes. These sections deal generally with matters not otherwise classified, and give an elementary account of these classes of compounds.

The reviewer has not referred at length to the descriptive portion of the work in so far as it concerns the preparation and constitution of synthetic organic substances, or to sundry theoretical questions, such as ring-strain, aromatic substitution, quinonoid structure, etc. This part of the work is very sound, and the whole book may be recommended to such as desire a good, up-to-date, rather advanced knowledge of organic chemistry. J. T. HEWITT

ADULTERATION AND ANALYSIS OF FOODS AND DRUGS. By J. F. LIVERSEEGE, F.I.C., Ph.C. Pp. xv+599. London: J. & A. Churchill. 1932. Price 36s.

Most Public Analysts and members of their staffs, and many other practical chemists, will quickly become enthusiastic concerning this book. It is written, by a well-known former Public Analyst, for all whose work lies in the same direction, and any of them would be proud to be its author.

It is a book conceived on a somewhat novel plan. As stated in the Preface, it gives an account of the analytical methods, research and memoranda, which have been found useful during forty-three years' experience in the Birmingham Municipal Laboratory. But the book does much more. It takes within its compass all those foods and drugs which normally come before a Public Analyst, and in systematic order surveys the official and unofficial standards and limits for each article, gives details of general composition, goes on to describe usual and unusual adulterants, and finally recommends methods of analysis which the author has found useful and satisfactory in working, and, in addition, gives many of the methods used by others. References to all important original papers are freely

included. So far, the scheme of the book is on the lines of many predecessors, but here the resemblance ceases. After a foreword by Mr. N. Chamberlain, a former Minister of Health, the author gives us three chapters on the administration of the Adulteration Act, with many cogent comments. The costs of prosecutions, effects of fines, number of samples taken for analysis by various local authorities, adulteration statistics, cost of administration, laboratory costs, methods of sampling and records are discussed at some length. Under the section dealing with laboratory staffs, the author comments as follows:—(Page 9) "a public analyst's laboratory is not a suitable place for training boys who 'have done well in chemistry' at school . . . . The work is too responsible to be entrusted to partly-trained students." With this opinion the reviewer is in complete agreement. The two chapters on sampling and records contain many references to, and comments on, important appeal cases. The chapters on Public Analysts' certificates and the evidence in prosecution cases are interesting and informative, and will prove of value to all who have to carry out work under any of the Acts relating to foods. But not every reader will agree with the author when he states his belief (p. 34), that "the analytical figures relating to a sample shall be the actual determinations of the one who signs the certificate," for in these days it would be very difficult in many busy laboratories to conform to this restriction. The Fertilisers and Feeding Stuffs Act, 1926, as the author rightly comments, allows of the analysis being made by another (not necessarily a *deputy* agricultural analyst) under the supervision of the agricultural analyst.

The chapters on "general methods of analysis" and "normal mineral constituents" clear the way for a detailed discussion in the following chapters of the separate articles of foods and drugs included in this volume: the list is a long and comprehensive one, and adequately surveys the whole field. There are also valuable chapters on colouring matters, metallic impurities, preservatives, methods of calculation and the microscopy of starches. At the end of the book the section on dispensing is timely and most valuable, especially to those having to examine and report on medicines dispensed from prescriptions. A most valuable feature of the work is the summary of important prosecutions, with references, which follows the sections on each food or drug.

An Appendix of 25 pages gives information on the standardisation of volumetric apparatus, preparation of solutions, conversion and other factors, milk calculations, alcohol tables, quantities of articles recommended to be purchased for analysis under the Adulteration Act, and examples of the reports and evidence in prosecution cases, together with other interesting data. There is an index of appeal cases cited, and a general index of 20 pages. There is an error (p. 222) in the statement of the result of the case of *Grigg* v. *Smith*, as the author has pointed out since publication, and "the appeal was allowed" should be read instead of "the conviction was confirmed."

It is impossible to speak too highly of this work. The whole scheme of the book is praiseworthy, and it has been carried out in such a way as to produce a most readable, eminently practical and valuable work of reference for the laboratory and the library. In spite of the multiplication of books, this volume will be much in demand, for the author's long experience makes him a reliable guide on the

matters of which he writes. The book is full of practical suggestions for making the Public Analyst a more efficient public servant, and our Society and all Public Analysts will be greatly indebted to its author. There are very few misprints. The book is well produced, and clearly printed on good paper, and because of its value one regrets that it has not been possible to issue it at a lower price.

ARNOLD R. TANKARD

QUANTITATIVE CHEMICAL ANALYSIS. By CLOWES and COLEMAN. Thirteenth Edition, Revised and Enlarged, by D. STOCKDALE, M.A., Ph.D. (Cambridge), A.I.C., and J. DEXTER, M.A., B.Sc. (London), A.I.C. Pp. xiv+605 (of which Tables 47 pp. and Index 13 pp.), 133 Illustrations and Diagrams. Twenty-ninth thousand. London: J. & A. Churchill. 1931. Price 18s. net.

This well-known work, first published in the year 1891, passed through twelve editions under the direction of the original authors, Dr. Frank Clowes and Mr. J. Bernard Coleman. The new edition has been revised by Dr. D. Stockdale, who has been mainly concerned with the inorganic portion, and Mr. J. Dexter, who is chiefly responsible for the organic parts of the book.

The revisers were confronted with a delicate task which they have discharged with great success; while preserving the admirable features and arrangement of the original work, they have exercised some judicious pruning. This has enabled them to make many important additions, without unduly enlarging the book, which they have brought thoroughly up-to-date.

The pruning has been effected by condensing the Table of Contents, thereby effecting a saving of several pages, by deleting a few of the older processes of analysis, and by avoiding repetition of details as much as possible. The numbering of paragraphs has been dispensed with; so, too, the Table of Separations, which is referred to now in the index. These and similar changes have enabled the revisers to insert many new processes and to describe new apparatus, all of which are now in use; the new edition contains thirty more pages than the last, but this addition is by no means a measure of all the fresh matter which has been added or substituted.

To decide what can be omitted always presents difficulty, and we regret, in particular, the omission from the new edition of the "Examples of Examination of Oils and Fats," pp. 424 and 425 of the last edition, and of some of the "Typical Analyses," namely, those on pp. 519–522 of the last edition. Students and analytical assistants have always found these very helpful, and, indeed, we have often thought that there is room for a book devoted entirely to these matters, which would be of the greatest assistance to both students and practitioners.

We would have welcomed the substitution of "determination" for "estimation" and "determine" for "estimate." *Estimation* is used throughout the book, except when dealing with vapour densities and molecular weights, in which cases the *determination* of these is referred to. To be consistent, *determination* should be used also in reference to *all* processes of quantitative analysis, for these operations are no less exact than those employed for the determinations of vapour densities and molecular weights. The word *estimate* is generally associated with the

approximate cost of work to be done by the builder or plumber (who in the end we generally find exceeds his original estimate), and in chemical work its use should be limited to those processes which are not susceptible of great accuracy.

Part I is concerned with General Processes of Chemical Analysis; Section 1 deals with the Chemical Balance, weights and weighing; Section 2 with some physical determinations; Section 3 with general analytical operations. Among other new matter the chainomatic balance, alundum and Jena crucibles are described.

Part II, Section 4, deals with Simple Gravimetric Estimations; among the additions in this edition may be mentioned the determination of copper with thiocyanate, and of nickel with dimethylglyoxime, and the use of Devarda's alloy in the determination of nitrates.

Part III, Volumetric Analysis. Section 5 deals with the apparatus and its calibration; indicators; standard solutions; Section 6 with alkalimetry and acidimetry; Section 7, oxidation—reduction reactions; Section 8 with unclassed methods. Among the additions in this part are the *p*H ranges of indicators, the uses of standard solutions of barium hydroxide, potassium iodate and titanous chloride, the employment of internal indicators in the titration of iron with potassium dichromate, and of zinc with potassium ferrocyanide.

Part IV, Section 9 (Miscellaneous Methods of Analysis), deals with electrolytic, electrometric, spectrometric and colorimetric methods of analysis.

This is an entirely new section, and the scattered electrolytic and colorimetric operations of the former edition have been collected and dealt with as distinct processes of analysis. The measurement of p_H by indicators and by electrometric titration is dealt with in this part.

Part V is concerned with General Quantitative Analysis, and Section 10 deals with Technical Inorganic Analysis—analysis of ores, alloys, iron and steel, coal and coke, phosphatic manures, and dry assaying, and there is a very useful addition upon the sampling of ores and alloys. Section 11 is devoted to Water Analysis, collection and inspection of the samples, and discussion of the results of analysis; Section 12 treats of Technical Organic Analysis—of foods, tanning materials and soap; the analysis of milk, butter, alcoholic beverages, sugar and tea is dealt with.

Lane and Eynon's method for determining reducing sugars is added, and McNichol's and Wolff's methods for the determination of resin acids in soaps are substituted for Twitchell's process.

On page 395 the following statement occurs in connection with Gerber's method for the determination of milk fat: "As an ordinary routine process this method is the simplest and quickest, but it is well to check its results by some standard method, such as Adams." In the reviewer's personal opinion the inference which the authors wish to be drawn—that this method is lacking in accuracy —cannot be admitted, for it has again and again been proved that Gerber's process is not only rapid, but extremely accurate, provided the pipette and tubes are accurately calibrated and the details of the process duly followed. One would be pleased if there were more analytical processes like Gerber's, capable of equal accuracy and rapidity of execution.

On pages 401 and 402, dealing respectively with the detection of preservatives in milk and butter, the following passages occur:—"Certain substances are

occasionally introduced into milk, more especially during hot weather, in order to prevent it from undergoing change," and in the case of butter, "If preservatives are detected, it may also be necessary to estimate the amount of boric acid which is present either as such or as borax"; it would have been an advantage if it had been stated that according to the Public Health (Preservatives, etc., in Food) Regulations, 1925, no addition of preservatives of any kind to milk or butter is permitted.

Section 13 deals with the examination of Animal and Vegetable Oils, Fats and Waxes, and an addition has been made in this edition in the examination of mineral oils and waxes.

Part VI, Section 14, is devoted to Organic Analysis; Section 15 deals with the Determination of Molecular Weights; Stepanov's method for the determination of the halogens has been added.

Part VII, Section 16 (Volumetric Estimation of Gases) includes calculation and calibration; Hempel's gas apparatus, Lunge's nitrometer; carbon dioxide by Pettenkofer's method; vapour density determinations.

Part VIII comprises tables for reference; results of typical analyses; tables of useful constants; list of common reagents, and their strengths, list of books for reference, index, factors for gravimetric analysis, antilogarithms and logarithms.

In this part there are a considerable number of changes in this edition—we have referred earlier to the omission of many of the results of typical analyses; among the additions are Clark and Lubs' table of standard buffer solutions, and W. Schloesser's table for the calibration of volumetric apparatus.

Chappuis' table of expansion of water is substituted for Kopp's, and Thiesen and Scheel's table of pressure of aqueous vapour replaces Regnault's.

The logarithm tables in this edition are printed in bolder type, which is a great advantage.

The index is considerably enlarged and is very full, but it is unfortunate that it is neither at the beginning nor at the end of the book, but is followed by fifteen pages of tables, which makes it a little difficult to find. In future editions we would suggest the avoidance of the repetition of the titles in the index (for instance, "lead" is once repeated), which makes reference more difficult, and might cause one to miss the earlier references.

The book is very free from typographical errors, but on pages 240 and 241 there are some misplacements of type, and on p. 66 there is a particularly unfortunate error, where, in dealing with the accuracy to be expected in the results of determinations, a tolerance of $\pm 0{\cdot}2$ per cent. is suggested, but in the numerical example the variation from the truth is $+0{\cdot}21$ per cent., and $-0{\cdot}19$ per cent.

Instead of the familiar black cloth binding of the former editions, this is bound in dark blue cloth, a pleasant change, and in accord with the times, when even the masterpiece in our literature is to be had in attractive coloured bindings instead of the customary black.

The revisers, in the preface, make the modest statement: "We concluded that no major changes in arrangement were necessary, and, therefore, confined ourselves to comparatively minor alterations and additions to the text," and on the title page they describe their work as "An Intermediate Text-Book." The

additions are far more important and numerous than these indications would lead one to expect, and the book in its present form even better fulfils the claim, on the title page of the previous edition, that it is "Adapted for use in the laboratories of Colleges, of Technical Institutes, and of Analysts," to all of which uses we strongly recommend this work, and wish it the world-wide acceptance enjoyed by the former editions. H. CHARLES L. BLOXAM

THE ESSENTIALS OF BACTERIOLOGICAL TECHNIQUE. By R. F. HUNWICKE, B.Sc., A.I.C. Pp. 108. London: Williams & Norgate, Ltd. Price 8s. 6d. net.

Interest in the study of bacteriology has been greatly stimulated of recent years by the introduction of improved methods of food manufacture and handling, and by the public discussions which have taken place from time to time on the importance of food hygiene. So far, students of bacteriology, as apart from pathology, have almost invariably had to turn to American publications to supply their needs, frequently with unsatisfactory results. Mr. Hunwicke has given us a book, based on his own studies and experience, which can be taken as a reliable guide by students in the bacteriological laboratories of this country.

The first two chapters deal with laboratory equipment and apparatus, and each section is written in a clear, concise manner which will be of considerable help to students—many of whom, unfortunately, trouble too little about this part of the subject. On p. 18, No. 1 of the instructions for working autoclaves should, perhaps, be "See that there is sufficient water in the autoclave."

The next section deals with culture media and methods of cultivation. A sufficient number of formulae for media is given to enable the student to do practically any type of work that is required in an ordinary bacteriological laboratory. It would have been advisable, perhaps, to explain more fully why certain media should not be autoclaved, and that a percentage of the tubes of media sterilised by the intermittent method on three successive days should be incubated in order to test the efficiency of sterilisation. This chapter ends with useful directions for standardising media to the required p_H value.

The methods of cultivation and study of micro-organisms, together with the examples of typical organisms, should enable the student to proceed to the systematic detailed study of micro-organisms.

The chapter on anaerobes is quite skilfully dealt with, but the reviewer does not like the summary way in which the pyrogallol-soda method is dismissed; he has obtained excellent results with this method. In somewhat inexperienced hands the McIntosh-Fildes jar may give very unsatisfactory results, and even the author himself does not have absolute faith in it, since he suggests supplementing its use with that of pyrogallol-soda.

In the next chapter, on microscopy and staining methods, the student is not worried with a lot of unnecessary formulae, but is given the essential staining methods in a simple and straightforward manner. It is pleasing to note the author's insistence on the constant microscopic examination of cultures.

The chapter on the examination of Milk and Milk-Products appears to have been a little hastily written. It would be advisable to give the official Ministry of Health methods where available, and in future editions to embody any alterations

which may have been made in the meantime. The reductase test, to which reference is made in this chapter, is used very largely in America, as well as Europe, and great store is set on it as an indicator of the keeping quality of milk. It is also found to be of great assistance, in conjunction with the fermentation test, in sorting out "gassy" milks.

In the Condensed Milk Section, p. 75, the statement that "reliance is placed on the high viscosity of the product, due to the addition of cane sugar, to prevent bacterial multiplication" is very debatable. The reason usually given is that multiplication is prevented by the concentration of the cane sugar present.

The chapter on the examination of water deals quite effectively with the methods, and a wise reference to Savage's *Bacteriology of Food and Water* will point to the student the way to follow up the work already done.

The book finishes with interesting chapters on "Meat and Canned Foods," "Vaccines, Diagnosis, Testing of Disinfectants, and Animal Inoculations."

In conclusion, Mr. Hunwicke must be congratulated on his work. The reviewer has tested many of the methods strictly according to the directions given in the book, and with very satisfactory results. He can cordially recommend the book to all students of bacteriology. J. D. ROBERTS

COLLOID CHEMISTRY—THEORETICAL AND APPLIED. By Selected International Contributors. Collected and Edited by JEROME ALEXANDER. Volume IV. Second Series of Papers on Technical Applications. Pp. 734. New York: The Chemical Catalog Company, Inc. 1932. Price $11.50.

Volume III of this series was reviewed in THE ANALYST (1932, **57**, 203). In the Preface to the present volume, Mr. Alexander states that, although in the preface to Volume I, published in 1926, there was mention of 175 promised papers, actually the four volumes contain 202.

Volume IV contains eleven papers on Carbohydrates (including Cellulose, Wood, Paper, Explosives, Sugar, Starch Products, and Sizing); Dyeing, three; Rubber, including Latex and Carbon Black, four; Plastics, three; Tanning, three; Photography, three; Coatings (including Paints, Colour Lakes, and Electro-Deposition), six; Foods, four; Laundry and Dry-Cleaning, two; Solidified Alcohol and Fire Extinguishers, two; Water Supply and Sewage Disposal, two. Thus, a very comprehensive range is presented. Well-known experts such as Samec, Mardles, Bancroft, Sheppard, Paine, Stiasny, McLaughlin, Emslander and Zakarias, to name but several, handle subjects in which they have made notable progress themselves. The world's universities and technical institutions have evidently been combed to secure the right men for the particular field under discussion.

The reviewer, being particularly interested in the subjects of foods, emulsions, proteins and wetting phenomena, has read twenty-three of the forty-two chapters with close attention, and has no hesitation in stating that the book is excellent. The subject-matter is clearly stated, and the summaries are authoritative. Unfortunately, owing, no doubt, to the difficulty of synchronising the receipt of papers from such widely separated sources, most of the papers are not really up to date. The reviewer's own paper was contributed in 1926, and was revised in

1930. The account of Tanning, contributed by Prof. H. R. Procter, does not indicate that this distinguished scientist died in 1927.

The reading of proofs has, on the whole, been good, but quite a number of errors have crept in. Thus, the sinusoid formula on p. 168 should read $y-a=b \sin(\sigma-\beta)+c \sin n(\sigma-\beta_1)$; H^- for H^+ on pp. 173 and 174; reference 44 on p. 576 gives Kolloid-Z. as volume 15 instead of 50. The index (p. 702) quotes Gibbs, and Gibbs, J. Willard; they relate to the same author. A number of minor spelling errors also occur.

It is permissible now to refer to Alexander's monumental task as covered by the four volumes. Taken together, they cover the field of academic and technical colloid chemistry more thoroughly than any other work. Their inclusion in any library devoted to technical chemistry, whatever its special aim, is essential. A veritable mine of information is presented, supported by thousands of references to the original literature, and the full author- and subject-indexes leave nothing to be desired. Editor and contributors alike are to be heartily congratulated.

WILLIAM CLAYTON

Publications Received

THE BRITISH PHARMACOPOEIA, 1932. Advance copy. The General Medical Council. To be published at 21s. net.

PERKIN AND KIPPING'S ORGANIC CHEMISTRY. Part I. By F. S. and F. B. KIPPING. London: W. & R. Chambers, Ltd. Price 4s. 6d. net.

CHEMISTRY AT THE CENTENARY (1931) MEETING OF THE BRITISH ASSOCIATION. Cambridge: W. Heffer & Sons Ltd. 1932. Price 7s 6d. net.

CHEMICAL ENGINEERING AND THERMODYNAMICS APPLIED TO THE CEMENT ROTARY KILN. By GEOFFREY MARTIN, D.Sc., F.I.C. London: Crosby, Lockwood & Son. Price 31s. 6d.

EXPLOSIVES. Second Edition. Vol. III. By ARTHUR MARSHALL. London: J. & A. Churchill. 1932. Price 42s.

AUSGEWÄHLTE UNTERSUCHUNGSVERFAHREN FUR DAS CHEMISCHE LABORATORIUM. By L. WINKLER. Stuttgart: F. Enke. Price RM. 19.5 (bound).

ORGANIC SYNTHESES. Vol. XII. London: Chapman & Hall. 1932. Price 10s. 6d. net.

CHEMICAL ENCYCLOPAEDIA. C. T. KINGZETT. Fifth Edition. London: Baillière, Tindall & Cox. 1932. Price 40s. net.

PREPARATION OF PURE INORGANIC SUBSTANCES. By E. H. ARCHIBALD. London: Chapman & Hall. Price 23s. net.

BRITISH STANDARD SPECIFICATIONS FOR XYLOLES (No. 458). British Standards Institution, 28 Victoria Street, London, S.W.1. Price 2s. net, post free 2s. 2d.

SAND, CLAYS AND MINERALS. A Magazine devoted to Economic Minerals. Published quarterly. By A. LEWIN CURTIS. Chatteris. Price 5s. per annum.

KINGSTON'S STERLING FLUCTUATION TABLES (as Measured in Currencies on a Gold Standard). Second edition. Kingston's Translation Institute, 96, Leadenhall Street, E.C.3. Price 1s. 1d. post free.

STANDARD SAMPLES, GENERAL INFORMATION. Circular No. 396 of the Bureau of Standards, U.S. Dept. of Commerce. 1932.