

THE ANALYST

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

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 5th, Mr. E. Richards Bolton, F.I.C., President, being in the chair.

Certificates were read for the first time in favour of Messrs. Leslie V. Cocks, A.I.C., Frederick Dixon, B.Sc., A.I.C., David Michael Freeland, A.I.C., Desmond Geoghegan, Claudius George Hyde, A.R.C.S., F.I.C., Vernon James Tilley, F.I.C., Leonard Wild, B.Sc., Hugh A. Williams.

Certificates were read for the second time in favour of Messrs. Charles Edwin Corfield, B.Sc., F.I.C., Harold E. C. Powers, B.Sc., A.I.C., John David Rogers, and Abraham Samson, A.R.C.Sc., A.I.C.

The following were elected Members of the Society:—Frederick Cecil Bullock, B.Sc., A.I.C., Thomas Harold Fairbrother, M.Sc., F.I.C., Ralph Skinner Rack, and Samuel George Sherman.

The President announced that the next meeting of the Society, on November 2nd, would be held, by invitation of the Pathological Institution of St. Mary's Hospital, in the theatre of that Hospital.

The following papers were read and discussed:—"The Oil of *Centrophorus Granulosus*," by A. Chaston Chapman, F.I.C., F.R.S.; "Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates. IX The Separation of Titanium from Tantalum and Niobium," by W. R. Schoeller, Ph.D., and E. C. Deering, B.Sc.; and "The Determination of Aldose Sugars by means of Chloramine-T, with Special Reference to the Analysis of Milk Products," by C. L. Hinton, F.I.C., and T. Macara, F.I.C.

The Berthelot Centenary.

Mr. A. CHASTON CHAPMAN, F.R.S., represented the Society on the occasion of the celebration of the centenary of the birth of Berthelot, on October 23rd-26th, 1927, in Paris, and presented the following address on their behalf:—

THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

TO

LE COMITÉ MARCELIN BERTHELOT.

We, the President, Council and Members of the Society of Public Analysts and other Analytical Chemists, the eldest offspring of the Chemical Society, wish to add our tribute of homage to that paid by the parent Society to the memory of the world-renowned Berthelot, on the occasion of the Centenary of his birth.

The discoveries in pure Chemistry, made by the pioneers of the science, have alone made possible the striking advances of the last half century in Analytical Chemistry, and among the names of these great pioneers that of Berthelot stands out prominently.

We should like, therefore, to join with you, his fellow countrymen, in honouring one to whom all chemists, whether investigating the principles of the science or engaged in its practical application, owe a lasting debt of gratitude.



*Signed on behalf of the Society of Public Analysts
and other Analytical Chemists,*

E. R. BOLTON,
President.

LONDON, *October 14th, 1927.*

Death of a Member.

With deep regret we record the death, on October 4th, of Reginald Charles Pakes.

Obituary.

BENJAMIN ARTHUR BURRELL, F.I.C., 1859-1927.

THE name of Burrell will always be associated with that of Thomas Fairley, one whom we senior men will ever hold in affectionate remembrance. The association began early, as Burrell studied Chemistry under Fairley at the Leeds Grammar School, and later became his chief assistant. There was a break of seven years (1893-1900), when Burrell acted as Public Analyst for Cork.

In 1912 came a definite partnership, only dissolved by the death of Fairley in 1919. In due course Burrell became Public Analyst for Leeds, the North Riding of Yorkshire and Scarborough, and Official Agricultural Analyst for the North and West Ridings of Yorkshire. In addition, he obtained appointments as Gas and Water Examiner.

The exigencies of our profession made such increasing demands upon our colleague that he found but little time for research, but he contributed papers to various journals including *THE ANALYST* and the journals of the Chemical Society and Society of Chemical Industry. He also published papers upon spa waters and atmospheric pollution, and, in conjunction with Fairley, a paper on bismuth in the human brain. As a result of public work on spa waters he obtained a considerably widened and extended practice.

A careful and steady worker, Burrell was always to be found in his laboratory, ready to give advice from a store of knowledge slowly and patiently acquired. Of unassuming demeanour and a modest disposition, he was not cut out for giving expert evidence. His truth-loving and scientific mind precluded him from excelling as the lawyer's typical "Expert." From personal experience I can testify that Burrell was so fair that, while acting for the prosecution on certain occasions, he was quoted as having given evidence for the defence. This is as it should be; although legal luminaries, seeking to win at all costs, may frown and fume.

Burrell was at his best as an instructor of classes at the Institute of Science, and in his own laboratory. He set up for himself, and tried to inculcate, the highest ideals. Whilst mistakes might be tolerated in some professions, an analyst, he held, must never be guilty of error, which in some cases might have far-reaching and disastrous consequences.

He rendered valuable assistance to the Yorkshire Section of the Society of Chemical Industry, of which he was Honorary Secretary from Mr. Fairley's death till he became Chairman in 1925: a post which he occupied up to his death.

He also acted as Honorary Secretary to the Yorkshire Analysts, who usually meet quarterly at Leeds. Over lunch and afterwards we were well able to appreciate our colleague's kindness and capability, and we shall miss him exceedingly. Our friend was working to the last. At the age of 68 he never hinted at retirement. Possibly he was happiest in his work.

At all events, Burrell has left a fine record of faithful and capable service cheerfully rendered to the community.

F. W. RICHARDSON.

The Oil of *Centrophorus Granulosus*.

By A. CHASTON CHAPMAN, F.I.C., F.R.S.

(Read at the Meeting, October 5, 1927.)

IN my earliest experiments on shark liver oil, which resulted in the discovery of an unsaturated hydrocarbon to which I gave the name "spinacene," the oil from two species of shark was employed. These oils were obtained from Portugal, where the two fish in question are known as "Barroso" (*Centrophorus granulosus*) and "Carocho" (*Scymnus lichia*), respectively.

About the same time, and unknown to me, Tsujimoto was working upon the same subject in Tokio, and a few weeks before the publication of my first paper, he published (*J. Ind. Eng. Chem.*, 1916, 8, 889) a preliminary communication describing a similar hydrocarbon to which he gave the name of "squalene." Since then this subject has received a great deal of attention in this laboratory, in Japan, and much more recently in the Organic Laboratory of the University of Liverpool, as well as by MM. André and Canal in Paris. As a result of these investigations it would seem that the problem is even more complex than was at first thought to be the case, and there is still room for difference of opinion as to the molecular formula of the hydrocarbon, to say nothing of its actual structure. All available evidence seems to suggest the identity of the two hydrocarbons, but even this cannot be considered to have been finally established. Since the publication of my last paper (*J. Chem. Soc.*, 1923, 123, 769) a little more work on the hydrocarbon has been done, and although it is not the object of this communication to deal with this, it may be a convenient opportunity to refer very briefly to it.

ACTION OF OZONE.—In my earlier experiments this was tried, but the ozoniser then at my disposal was not sufficiently powerful, and the experiments have only been comparatively recently repeated. It will suffice to say that, so far as this work went, it showed that the products formed by decomposition of the ozonide were very similar to those recorded by Majima and Kubota in their similar work on squalene.

ACTION OF CHROMYL CHLORIDE.—Chromyl chloride was found to yield two derivatives in carbon disulphide solution by the addition of 4 or 8 molecules of CrO_2Cl_2 , but no further addition could be effected. The main decomposition product was, however, too resinous to be of use in suggesting a structure of the hydrocarbon.

Having regard to the unexpected result obtained in the isolation of this very unsaturated hydrocarbon from this particular oil, it was felt that it might be desirable to look rather closely into the glycerides, alcohols and other substances

representing the balance of the oil, as it was thought that there might be something equally unusual in these. The oil used in these experiments was specially supplied to me as "Barroso" oil (that is to say, the oil of *Centrophorus granulatus*) by Messrs. Abecassis (irmaos) & Cia of Lisbon, and I have no reason to doubt that it did consist of that oil.

The bulk of the spinacene was first removed from a quantity of the oil (about 5 litres) by distillation at 3–4 mm., and the residue saponified with alcoholic potash. The soap solution was then extracted with ether, and the white viscous residue from the ether diluted with alcohol. From this a quantity of cholesterol was obtained, but it was evident that there was present another substance somewhat less soluble in alcohol. By a process of recrystallisation this was obtained in the form of extraordinarily lustrous crystals, melting sharply at 69°C., and possessing the general properties of an alcohol. Tsujimoto and Toyama (*Chem. Umschau*, 1922, 29, 27–9, 43–5), have described a similar alcohol obtained from several Japanese shark liver oils and have named it *batyl alcohol*. This melts at 69° C. and was stated to have the formula $C_{20}H_{42}O_3$, though Toyama subsequently (*Chem. Umschau*, 1924, 31, 61–7), suggested $C_{21}H_{44}O_3$ as being more exact.

The alcohol obtained in my experiments gave, on combustion, the following results:—Carbon, 73.0 per cent., hydrogen, 12.7 per cent. ($C_{20}H_{42}O_3$ requires 72.7 per cent. C and 12.7 per cent. H, and $C_{21}H_{44}O_3$ requires 73.2 per cent. C and 12.8 per cent. H). There can, therefore, be very little doubt that this alcohol is identical with that obtained by the Japanese workers, but the analysis is not of material assistance in deciding between the above two formulae.

The liquid from which the cholesterol and batyl alcohol had been separated consisted chiefly of a liquid alcohol, but it could not be freed from spinacene even by distillation after esterification by means of acetic anhydride. As it was found to be impossible to prepare a pure specimen of this liquid alcohol, a small quantity, contaminated with about 10 per cent. of spinacene, was hydrogenated, using platinum black, and an excellent yield of a solid alcohol was obtained which, after two recrystallisations from alcohol, melted at 68°–69° C. From this it was evident that the liquid alcohol is selachyl alcohol, $C_{20}H_{40}O_3$ or $C_{21}H_{42}O_3$, first prepared by Tsujimoto and Toyama (*loc. cit.*), and which, according to these workers yields batyl alcohol when hydrogenated under the above conditions. It should be stated that an amount of glycerol was obtained corresponding with about 0.5–0.6 per cent. on the original oil. This is contrary to the experience of Marcelet, who stated (*Bull. de L'Inst. Océanographique*, 1920, 368) that these fish oils were generally free from glycerol.

FATTY ACIDS.—These were liberated from all available soap solutions, that is to say, the solutions from which the above-mentioned alcohols had been separated as completely as possible. After having been separated they were converted into methyl esters which, in turn, were submitted to a prolonged process of fractionation under a pressure of 3 or 4 mm. Inasmuch as the acids consisted of both saturated and unsaturated members of several series, this process of fractionation

could not be carried very far owing to the formation of constant boiling mixtures, and to the effect of the esters of the one series on the boiling points of those of the other. Other methods of separation were then tried, and eventually large amounts of the solid saturated members of the series were obtained, melting between 61° and 62° C., and consisting mainly of stearic and palmitic acids. The unsaturated acids of the series were obtained by extracting the lead salts with ether, methylating the acids of the soluble salts and fractionating through a long column at a pressure of 3.5 to 4.5 mm. In this way a series of fractions boiling from 140° to 200° C. was obtained, the greater part distilling between 160° and 180° C. The iodine value and saponification value of this fraction showed it to consist mainly of methyl oleate. The amount of material above 180° C. was too small for investigation, and still contained a proportion of methyl oleate. After saponification, the resulting semi-solid acid was found to have a lower iodine value than oleic acid. A small amount of a monobasic acid with a molecular weight of about 340 was indicated, and may quite possibly have been the selacholeic acid, $C_{24}H_{46}O_2$, described by Tsujimoto (*J. Soc. Chem. Ind. Japan*, 1925, 28, No. 8.) This liver oil, therefore, contains, in addition to the unsaturated hydrocarbons, cholesterol, batyl and selachyl alcohols and glycerol, together with stearic, palmitic and oleic, and possibly smaller proportions of other saturated and unsaturated fatty acids. From this it would appear that in respect of non-hydrocarbon constituents the liver oil of the *Centrophorus granulosus* is very similar in composition to that of certain other shark liver oils which have been studied and described by Tsujimoto and others.

From the purely analytical point of view the study of this oil has been of importance as affording a striking example of the impossibility, in many cases, of separating the hydrocarbon and alcoholic constituents of oils—that is to say, the so-called unsaponifiable matters—from the soaps produced by the saponification of the esters. The former are generally soluble to a very appreciable extent in the latter, and cannot be removed completely, even by repeated extraction with immiscible solvents. It is, therefore, very easy to obtain too low a result for the percentage of unsaponifiable matters, and, at the same time, it is impossible to obtain the alcohols in a state of sufficient purity to admit of their complete identification. These difficulties have been experienced by others who have worked with these liver oils, and are specially referred to by Drummond, Channon and Coward (*Biochem. J.*, 1925, 19, 1047).

My best thanks are due to Miss F. M. G. Micklethwait, M.B.E., F.I.C., and to Mr. J. J. Scanlan, A.R.C.Sc.I., A.I.C., for their help in connection with this investigation.

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

IX. The Separation of Titanium from Tantalum and Niobium.

By W. R. SCHOELLER, Ph.D., AND E. C. DEERING, B.Sc., A.I.C.

(Read at the Meeting, October 5, 1927.)

THE separation of titanium from tantalum and niobium is still one of the most baffling problems of mineral analysis, despite the prolonged labours of a number of able investigators. The proposed methods, and the controversies to which they gave rise, form a fairly extensive literature, in a study of which we have been engaged for some time past. A critical review of the more recent methods, based chiefly on our own tests and in part on the work of other observers, constitutes the first part of this paper. The second part contains the preliminary notice of a new separation method, discovered in 1923. The separation achieved by it is still rather approximate; further work is now in progress, but the investigation is likely to be a protracted one, owing to its tedious nature and the limited time at our disposal. By the present publication we wish to secure priority, as well as make a temporary contribution, believed to have a certain practical value, until a more accurate method is available.

PART I. OBSERVATIONS ON THE MORE RECENT LITERATURE.

A. HALL AND SMITH'S INVESTIGATION (1905).—The work of Hall and Smith,¹ though not primarily analytical, forms a convenient starting-point for this inquiry. Being engaged in the preparation of pure niobium compounds, they considered it "most important to find some means of estimating the amount of titanium" in their products. Certain reactions, which need not here be described, were unsuccessfully investigated, with the result that the position remained as it was at the close of last century; no accurate separation method was known, but titanium could be detected and determined colorimetrically in presence of tantalum and niobium by means of hydrogen peroxide.

B. PUBLICATIONS BY HAUSER AND CO-WORKERS (1908–1912).—As far as we have been able to ascertain, the methods used by Hauser in his analyses of certain titano-niobates have never been re-investigated or criticised; but the internal evidence afforded by his writings shows that he subsequently modified his original process, and finally abandoned it for no stated reason.

(a) *Hauser on risörite*.²—The hydrolysis precipitate from the bisulphate fusion is dissolved in a solution of mannitol and potassium hydroxide. This solution, poured into moderately strong sulphuric acid, gives a precipitate consisting of earth acid; the titania in the filtrate is precipitated with ammonia.

(b) *Hauser and Finkh on plumboniobite*.³—The procedure outlined for risörite is followed, but the earth-acid precipitate from the acidified mannitol solution is stated to be contaminated “with small quantities of titania,” for the extraction of which ammonium salicylate is used. “The separation of tantallic and niobic acid from titania is thus quantitative.”

(c) *Hauser and Herzfeld on blomstrandine*.⁴—The hydrolysis precipitate is subjected to treatment with alkaline mannitol solution as before, but this time the titanium precipitate, as well as the earth-acid fraction, are treated with “basic” ammonium salicylate. The separation is “accurate to within a fraction of one per cent.” For the subsequent separation of tantalum from niobium, the oxides are fused with potassium hydroxide and the resulting solution treated with carbon dioxide, which is stated to precipitate niobic acid, but not tantallic acid. In a later paper, however (more fully discussed under C below), Hauser and Lewite⁵ show that the carbon dioxide treatment produces a colloidal suspension of the earth acids, the first to flocculate being the tantallic acid sol.

(d) *Meyer and Hauser's monograph*⁶ (sections on earth acids and titania by Hauser).—The complete analysis of blomstrandine is described and reference is made to Hauser and Herzfeld's paper (*vide supra*), but the scheme given differs from the original one in the following essential steps:—The hydrolysis precipitate is dissolved in sulphuric acid and hydrogen peroxide, lead sulphate and gangue filtered off, and the filtrate again hydrolysed, with addition of sulphurous acid (Weiss and Landecker's method)⁷; the precipitate is treated by Muller's salicylic acid method (see D) for the separation of the titania. The earth acids are separated from each other by Marignac's fluoride method, not by carbon dioxide (p. 303). In the same work (p. 275) the freshly precipitated earth acids are described as being readily soluble in caustic potash containing mannitol; the treatment is recommended for the elimination of traces of iron, but no mention is made of its applicability to the separation of the earth acids from titania.

We must conclude that Hauser discarded the mannitol method; but we considered an experimental investigation necessary before recording a definite opinion for or against it. The reagent used was a solution containing 10 per cent. of mannitol and 20 per cent. of potassium hydroxide. The mixed oxides (see Table I) were submitted to bisulphate fusion followed by the usual hydrolysis. The washed precipitate was treated with the mannitol reagent. In Exp. 5 no titania was present, and the precipitate dissolved in a few minutes. In all the other tests, the portion remaining insoluble appeared the larger the higher the proportion of titania in the oxide mixture; the filtered extracts, on acidification with sulphuric acid and addition of hydrogen peroxide, gave hardly any reaction for titania. As we could not obtain complete solution of the oxides to be separated, further work was given up. We are satisfied that mannitol does not effect a separation, and that Hauser must have reached the same conclusion. The valuable part of his work is the application of ammonium salicylate to the separation of titania

from the earth acids, probably an adaptation of Dittrich and Freund's⁸ method for the separation of titania from zirconia.

TABLE I.

Exp.	1.	2.	3.	4.	5.	6.
M_2O_5 , grm.	0.1007	0.1004	0.1000	0.1000	0.0510	none
TiO ₂ „	0.1005	0.1006	0.0510	0.0252	none	0.0504

C. THE WEISS AND LANDECKER CONTROVERSY (1909–1913).—A paper by Weiss and Landecker⁷ on the separation of tantalum, niobium and titanium caused a number of investigators to test and criticise the proposed method. Though the greater part of the controversy deals with the separation of tantalum from niobium, we propose to include it wholly in this section; it represents an important phase in the history of earth-acid analysis, and as such requires a brief review at some stage of this series of investigations.

Outline of Weiss and Landecker's methods.—(1) The oxides of the three elements are fused with sodium carbonate; sodium nitrate is added to the fluid mass, which is then cooled and leached with hot water. The residue consists of the greater part of the titania, the balance being precipitated in the filtrate by hydrogen sulphide. The earth acids are recovered from the acidified filtrate by ammonia precipitation; the precipitate is ignited and again fused with sodium carbonate and nitrate. The fused mass is treated with warm water, part of the tantalum remaining insoluble. The remainder is precipitated from the filtrate by treatment with carbon dioxide; niobic acid remains in solution.

(2) Another process for the separation of titania from the earth acids consists in dissolving the hydrolysis precipitate in acidified hydrogen peroxide and adding sulphurous acid till the liquid is decolorised; the earth acids are precipitated with a certain amount of titania. Several repetitions of the procedure are stated to result in a quantitative separation.

Criticisms—(a) *Of the titania and earth-acid separation by Ruff and Schiller.*⁹—Though the original directions were closely followed, no hydrogen sulphide precipitate could be obtained, and the earth-acid fraction gave as strong a titanium reaction as the original oxide mixture. Various modifications were next tried, but the composition of the oxide mixture remained substantially unaltered by the treatment. Marignac made a similar observation in studying the action of fused sodium carbonate on mixtures of titanitic and niobic oxides. In the hydrogen peroxide and sulphurous acid process, the quantity of sulphurous acid added was almost immaterial as regards precipitation of the earth acids. The only important factor was the acidity of the solution, as it determined the relative amounts of the oxides in the precipitate; but no separation could be effected.

Wells¹⁰ states that the method was abandoned, because "it was found that titanium passes into the soluble part with columbium and tantalum, just as it does when no nitre is used."

(b) *Of the tantalum-niobium separation.*—Wedekind and Maass¹¹ state that the method was used in the preparation of pure tantalic acid from fergusonite;

it is a partial success (*zum Teil gut bewährt*), but the most favourable conditions must be worked out by the operator himself. According to Foote and Langley¹² no separation was obtained in any test, the niobium being almost quantitatively co-precipitated in the carbon dioxide treatment. Hauser and Lewite⁵ assert that erratic results were obtained, but Foote and Langley's condemnation is considered too absolute. The pure sols of tantalic and niobic acids were prepared; the tantalic acid sol flocculates more quickly than that of niobic acid (*cf. B, c*). The sols being sensitive to electrolytes, the addition of nitrate to the fusion is not only unnecessary but actually harmful, as it causes premature flocculation of the niobic acid sol. Some tolerable results were obtained in the carbon dioxide process by fusion of the pentoxides with sodium carbonate alone; but Marignac's fluoride separation is always to be preferred for accuracy.

Meyer and Hauser⁶ (p. 294) find that the sodium tantalate residue tenaciously retains niobium, and, in spite of a repetition of the procedure, niobium can always be detected in the insoluble residue.—Meimberg and Winzer¹³ state that Weiss and Landecker's method, as well as the modification proposed by Hauser and Lewite, is unsuitable for analytical as well as preparative work.

In conclusion, the controversy over Weiss and Landecker's paper, whilst valuable as a contribution to the general knowledge of earth-acid analysis, resulted in a practically complete rejection of their methods. We submit, therefore, that no further experimental work is required, the results obtained by Weiss and Landecker not having proved reproducible.

D. MULLER'S METHOD.¹⁴—This consists in fusing the mixed oxides with 5 grms. of potassium carbonate, leaching the mass with water, and boiling the liquid with 15 grms. of salicylic acid for 3 to 4 hours. The precipitate is collected, washed with dilute salicylic acid solution, ignited, and re-treated as above, several times if required; re-treatment is necessary if the salicylic acid liquor becomes yellow in the boiling. The final pentoxide precipitate is fused with bisulphate, recovered by hydrolysis, ignited, and weighed. The combined salicylate filtrates are concentrated and boiled with ammonia, and the precipitate ignited and weighed as titania. The results of the published analyses are surprisingly good, the pentoxide and titania errors in 14 test separations being (with a single exception) well below 0.001 gm. The number of fusions required for a separation was from one to four, increasing with the amount of titania present.

In our six check tests tabulated below, the separation was done according to Muller's directions, but only two fusions were carried out in each case. The residue from the first fusion (R^1) was weighed as a guide and re-treated, giving R^2 ; this was purified by bisulphate fusion, solution in oxalic acid, and treatment with hydrogen sulphide. The small quantities of platinum sulphide and silica were filtered off, and the filtrate evaporated with sulphuric acid for the destruction of the oxalic acid. After dilution, the liquid was hydrolysed as usual. The weighed precipitate R^{2a} was then tested colorimetrically for titania (which was still present in every case), the difference giving pentoxide. In a preliminary experiment 0.1005 gm. of titania was treated by Muller's process without addition

of any earth acid; complete solution was obtained after three successive fusions and extractions.

TABLE II.

Exp.	1.	2.	3.	4.	5.	6.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
M_2O_5 taken	0.1007	0.1500	0.1006	0.1534	0.2004	0.2009
TiO_2 „	0.1050	0.0530	0.1005	0.0515	0.0105	0.0021
R^1	0.1150	0.1632	0.1138	0.1663	0.2046	0.2012
R^2	0.0993	0.1406	0.1000	0.1520	0.1967	0.1934
R^{2a}	0.0958	0.1359	0.0969	0.1497	0.1914	0.1859
TiO_2 in R^{2a}	0.0025	0.0043	0.0020	0.0015	0.0014	0.0005
M_2O_5 in R^{2a}	0.0933	0.1316	0.0949	0.1482	0.1900	0.1854
M_2O_5 error	-0.0074	-0.0184	-0.0057	-0.0052	-0.0104	-0.0155

What these figures express is, that we were unable to obtain the very perfect separation claimed by Muller; after one repetition of the treatment we were confronted in every case with a substantial loss of pentoxide before having achieved the quantitative removal of the titania. We must add that Muller's paper contains no details whatever regarding any precautions to be observed to ensure a good separation; a bare outline of his procedure is compressed into 12 lines of print. Thus, he does not state whether the final earth-acid fraction was tested for titania, and with what result. In our opinion, Muller's method is superior to all its predecessors, in that the fundamentally different behaviour, towards salicylic acid, of titania and of the earth acids persists when these oxides are in admixture; but the degree of accuracy of which the method was found capable falls far short of the ordinary analytical standards.

E. MELLOR'S PROCEDURE.¹⁵—The following directions are found in Mellor's *Treatise*:—The hydrolysis precipitate from the bisulphate fusion is extracted with ammonium sulphide, then dissolved in sulphuric acid and hydrogen peroxide. The solution is again hydrolysed, and the moist precipitate is "boiled three or four hours with a large excess of salicylic acid. The titanic oxide dissolves, while the niobic and tantalic oxides remain insoluble." The authorities quoted in a footnote are Dittrich and Freund⁸ and Hauser and Herzfeld,⁴ but these procedures are dissimilar to the one under discussion.

In proceeding to follow Mellor's directions, we found the precipitate produced by the hydrolysis of a titanic sulphate solution ("metatitanic acid") to be insoluble in salicylic acid or ammonium salicylate or both; the quantities of titania found in the extracts were of the order of 0.001 grm. In an attempted test separation, the washed hydrolysis precipitate from 0.0519 grm. of pentoxides and 0.0522 of titania was boiled for 3 hours in a bulk of 500 c.c. with 15 grms. of salicylic acid. The filtrate had a pale yellow tint, and the ignited precipitate weighed 0.1014 grm., or almost as much as the mixed oxides taken. No separation had taken place.

On the other hand, we established the interesting fact that the precipitate produced by ammonia in titanic sulphate solutions, whether hot or cold, is completely soluble in salicylic acid or ammonium salicylate, or both.

The effect of the presence of earth acids in the precipitate was next tried. The mixed oxides were fused with bisulphate, and the mass leached with dilute sulphuric acid (with mixtures rich in earth acid, ammonium oxalate was added so as to produce a clear solution). The liquid was made alkaline with ammonia, the precipitate collected and washed with dilute ammonium nitrate solution, and boiled with a solution of 5 grms. each of salicylic acid and ammonium salicylate for two hours. The precipitate was filtered off; the more or less deeply coloured filtrate was boiled with ammonia and filter pulp, and the precipitated titania ignited and weighed. Table III shows the results:—

TABLE III.

Exp.	Pentoxide taken.	TiO ₂ taken.	TiO ₂ found.
		Grm.	Grm.
1	Nb ₂ O ₅	0.1023	0.0802
2	do.	0.1030	0.0805
3	do.	0.1000	0.0778
4	(Ta, Nb) ₂ O ₅	0.1008	0.0419
5	do.	0.2014	0.0210
6	do.	0.3004	0.0148

The tests prove that the extraction of the titania is incomplete in one operation, and that the proportion extracted decreases with an increase in the quantity of earth acid. When the insoluble residue from the extraction was ignited and again treated as the original mixed oxides, more titania was extracted; but even a third treatment failed to effect its complete removal. Moreover, niobic acid did not remain altogether insoluble. The reaction is worth further research, which is in contemplation. For the present, we merely note that the salicylic acid treatment of a mixed hydrolysis precipitate, as prescribed by Mellor, fails to extract the titania therefrom.

Extraction of the mixed ammonia precipitate with other hydroxy acids (*e.g.* sulphosalicylic, gallic, and lactic) was also tried, but proved ineffective.

F. TODD'S PROCESS.—Todd¹⁶ published a process for the analysis of earth-acid minerals, in which the bisulphate-hydrolysis precipitate, after the customary elimination of silica by hydrofluoric acid, is fused with potassium carbonate. The fusion residue insoluble in water is once more fused with potassium carbonate, and the fused mass again leached. The combined extracts contain the earth acids, tin, and part of the titanium, which are precipitated by acidification. The precipitate, after having been extracted with ammonium sulphide, is ignited and weighed; a small portion is used for the colorimetric determination of the titania. The remainder serves for the volumetric determination of the niobium by Metzger and Taylor's method,¹⁷ a deduction being made of the permanganate consumption, in a separate test, of a quantity of titania equal to that found by colorimetry, under identical conditions of reduction. Tantallic oxide is computed by difference.

Fusion of the hydrolysis precipitate with potassium carbonate, as employed by Todd, is no doubt a useful means for freeing the earth acids from adsorbed

minor basic impurities; this applies to a precipitate practically free from titania. If much titanium is present, the solution of the major problem of separating titania is not advanced by the fusion; for not only does a substantial proportion of titanium find its way into the filtrate along with the earth acids, as Todd points out, but complete extraction of the earth (or, at least, tantalic) acid cannot be achieved even by several repetitions of the procedure; by then the greater part of the titania also is rendered soluble, with the result that the protracted manipulations have served no useful purpose. In Table IV, which gives the results of our fusion tests, R^1 denotes the residue from the extraction with water of the first potassium carbonate fusion, R^2 the residue from the fusion and subsequent extraction of R^1 , and so on. All the fusions were done with 3 grms. of carbonate. In Exps. 1 and 2, no earth acid was added.

TABLE IV.

Exp. 1.	TiO ₂ taken:	0.2515	gram.	TiO ₂ rendered soluble:	0.0017	gram.
do. 2.	„ „	0.2530	„ „ „ „	„ „ „ „	0.0013	„ „
Exp.		3.		4.		5.
		Grm.		Grm.		Grm.
Ta ₂ O ₅ taken		0.2528		0.2509		—
Nb ₂ O ₅ „		—		—		0.2519
TiO ₂ „		0.2510		0.2512		0.2514
R^1		0.2630		0.3115		0.0782
R^2		0.2003		0.1647		0.0702
R^3		0.1325		0.1328		0.0588(c)
R^4		0.1028(c)		0.1011(c)		—
TiO ₂ in final $R(a)$		0.0772		0.0800		0.0495
M ₂ O ₅ „ „ „ (b)		0.0256		0.0211		0.0093
						0.0540(c)
						0.0698
						0.0888
						0.2512
						0.2512

(a) By colorimetry. (b) By difference. (c) Purified oxides.

These tests prove that titania by itself remains insoluble after the potassium carbonate fusion. With an equal amount of tantalic oxide, the residue from the fourth fusion still contains a substantial amount of tantalum, whilst about two-thirds of the titania have been rendered soluble. With an equal quantity of niobic oxide, the residue from the third fusion may be almost niobium-free, but about four-fifths of the titania go into solution with the niobic acid. A comparison of the weights of R^1 , Exps. 3 and 4, with the corresponding figures in Exps. 5 and 6, shows how much more strongly the deportment of titania is affected by niobium than by tantalum.

Turning to Todd's volumetric determination of the three constituents of the oxide mixture, we must point out the weaknesses which, in our opinion, render it an unreliable substitute for a separation method. Todd states that he obtained concordant results by Metzger and Taylor's method,¹⁷ and he was able also to confirm their empirical factor (1 c.c. 0.1 N KMnO₄ = 0.007052 gm. Nb₂O₅) by means of a "nearly pure niobium salt." Wells,¹⁰ however, was unable to confirm

that factor, the figure found by him being 0.007767. Walker and Parsons¹⁸ ascribe these discrepancies to "the varying impurity of the standard employed for the titration, rather than to the method"; but subsequently Schoeller and Waterhouse (Section III¹⁹) obtained different and widely divergent factors (0.007424 and 0.008139) with the same preparation of pure niobic oxide, according to slight variations in the conditions of the reduction. The objections of Treadwell²⁰ and of Schoeller and Waterhouse against the published oxidimetric processes for niobium have not been answered. The late Dr. W. F. Hillebrand expressed himself as follows²¹: "I agree entirely with the conclusions reached by you (W. R. S.) and Mr. Waterhouse on the volumetric estimation of columbium."

Further complications are introduced by the presence of titanium, which forms a soluble complex in which, according to Treadwell,²⁰ more complete reduction of the niobium takes place; hence the use of Metzger and Taylor's factor, even if correct, is inadmissible for a mixed niobium-titanium solution. Again, the colorimetric method (included in Todd's process) is not sufficiently accurate for any but subordinate amounts of titania, and the degree of reduction of the niobic oxide may vary with the unknown $\text{Nb}_2\text{O}_5 : \text{TiO}_2$ ratio of the mixture under investigation. Dr. Hillebrand informed one of us²¹ that he made "some tests on the reduction of columbium together with varying amounts of titanium. If soluble complexes were formed they did not materially help the reduction of the columbium, for erratic results were obtained." We may safely conclude that the presence of titanium accentuates the uncertainty of the volumetric determination of niobium.

G. THE COLORIMETRIC DETERMINATION OF TITANIUM.—The uncertainties and contradictions that surround the subject under review are such that the colorimetric determination even of large quantities of titanium, though involving an error of, roughly, 10 per cent., is commonly regarded as more reliable than any attempt at an actual separation. Still, the fact remains that without a preliminary elimination of titania there can be no satisfactory separation of tantalum from niobium.

A number of contradictory statements are found in the literature as to the solubility of the earth acids in acidified hydrogen peroxide.²² The actual position may be summed up as follows:—The freshly precipitated earth acids are soluble in sulphuric acid and hydrogen peroxide,⁷ though tantalic is dissolved much less readily than niobic acid. Whilst, however, the solution of titanitic acid in hydrogen peroxide is essentially molecular, those of tantalic and niobic acids are distinctly colloidal,²³ the tantalic acid sol being more easily flocculated; hence it begins to separate after some hours' standing.²⁴

A re-investigation of the subject, as contemplated by Schoeller and Powell (Section I²⁵), need not be undertaken from the point of view of practical analysis, as there is no difficulty in obtaining a clear solution of the mixed oxides; not only is the mass from the bisulphate fusion soluble in hydrogen peroxide and sulphuric acid,²⁴ but tartaric or oxalic acid effects its rapid solution without interfering with

the colorimetric determination of the titanium by hydrogen peroxide.²⁶ We dissolve our bisulphate fusions in dilute oxalic acid, treating the colorimetric standard in the same manner.

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PART II. PRELIMINARY NOTICE OF AUTHORS' SEPARATION METHOD.

The experimental work recorded above shews salicylic acid or its ammonium salt to be relatively the most effective reagent so far discovered for the titania and earth acid separation, though the approach to accuracy leaves much to be desired. In our systematic search for a quantitative separation method, we were led tentatively to advance the proposition that precipitation from a solution of the mixed oxides is more satisfactory than extraction of a mixed precipitate. Now the number of common solvents for titania and the earth acids is small, being at present confined to hydrofluoric acid, acidified hydrogen peroxide, and certain organic acids, notably tartaric and oxalic acids. Of several separation schemes devised, the one given below was tested more thoroughly than the others, and it proved sufficiently promising to justify publication of this preliminary notice.

PROPOSED METHOD.—This is based on the dissociation of the soluble tartaric complexes of the metallic acids by a large excess of mineral acid, tantallic and niobic acids being precipitated; the titanic salt of the mineral acid remains in solution, from which it is hardly precipitated, even by more prolonged boiling. The following experiments illustrate the deportment of the earth acids under varied conditions:—The weighed oxide was fused with bisulphate, the cold mass

dissolved in a solution of tartaric acid (3 grms.), and the liquid (300 c.c.) boiled for 20 to 30 minutes with the quantity of strong mineral acid given in Table V. The precipitate was filtered off, washed with acidulated water, ignited, and weighed:

TABLE V.

Exp.	Taken.	Mineral Acid.	Recovered.	Error.
			Grm.	Grm.
1	Ta ₂ O ₅ 0.1017	30HNO ₃	0.1032	+0.0015
2	do. 0.1010	30HNO ₃ +15H ₂ SO ₄	0.0931	-0.0079
3	do. 0.1012	30HCl	0.1033	+0.0021
4	do. 0.1013	30HCl+15H ₂ SO ₄	0.0647	-0.0366
5	Nb ₂ O ₅ 0.1021	30HNO ₃	0.0960	-0.0061
6	do. 0.1023	30HNO ₃ +15H ₂ SO ₄	0.0606	-0.0417
7	do. 0.1011	30HCl	0.0940	-0.0071
8	do. 0.1009	30HCl+15H ₂ SO ₄	0.0672	-0.0337

The figures indicate complete recovery of tantalic acid, and a substantial recovery of niobic acid if no sulphuric acid is present. In the subsequent test separations, nitric acid was used as the precipitant. The precipitation of the earth acids was not quite quantitative, possibly due to the presence of sulphate ion (from the flux) or interference of titania. On the other hand, in accordance with the familiar behaviour of the precipitated earth acids, co-precipitation (adsorption) of titania takes place; this increases with the concentration of the metallic acids, and is counteracted by re-precipitation. The two errors are of opposite sign and tend to neutralise each other, so that seemingly close results may be obtained. In any case, the procedure is very simple and accomplishes a preliminary separation of the mixed oxides into an earth-acid fraction poor in titania and a titania fraction poor in earth acids. The final treatment of the two fractions will require a different process, *e.g.* some form of salicylate extraction; the problem is now under investigation.

THE SEPARATION.—The mixed oxides (0.1 to 0.2 gm.) are fused with 2 grms. of potassium bisulphate in a silica crucible. The cold mass is dissolved by digestion with a strong solution of 3 grms. of tartaric acid. The solution, diluted to about 300 c.c., is boiled with 30 c.c. of strong nitric acid for 15 to 20 minutes. After the boiling, the precipitate (*P*¹) is thoroughly mixed with filter fibre, washed with one per cent. nitric acid, ignited, and weighed; if the weight is about 0.1 gm. or more, the precipitate is again fused with bisulphate and the whole procedure repeated. The precipitate *P*² represents the earth-acid fraction.

The combined filtrates from *P*¹ and *P*² are evaporated with 10 to 15 c.c. of strong sulphuric acid, and the tartaric acid destroyed by cautious addition of nitric acid to the gently fuming mass till it is colourless. After cooling and diluting, a slight excess of ammonium is added; the precipitate is mixed with filter pulp, collected, washed with ammonium nitrate solution, ignited, and weighed as the titania fraction.

RESULTS OF TEST SEPARATIONS.—We are indebted to two of our collaborators, Messrs. C. Jahn and E. F. Waterhouse, for carrying out the tests marked with

their initials. The composition of the pentoxide used is indicated by the symbols in Column 1.

TABLE VI.

Exp.	M_2O_5 Grm.	Taken.		Deviation		$TiO_2(a)$ in P^2 . Grm.	Operator.
		TiO_2 . Grm.	P^1 . Grm.	P^2 . Grm.	P^2 from M_2O_5 . Grm.		
Ta 1	0-1010	0-1014	0-1207	0-1047	+0-0037	Lost	WRS
„ 2	0-1005	0-1010	0-1112	0-0960(b)	-0-0045	0-0010	„
„ 3	0-1007	0-1020	0-1136	0-1028	+0-0021	0-0040	„
Nb 4	0-1000	0-1006	0-1168	0-1000	0-0000	0-0030	„
„ 5(c)	0-1090	0-1555	0-1224	0-1038	-0-0052	0-0036	CJ
„ 6(c)	0-1052	0-1520	0-1274	0-1006	-0-0046	0-0028	„
„ 7(c)	0-3908	0-0330	0-4016	0-3900	-0-0008	0-0240	„
„ 8(c)	0-3996	0-0341	0-4063	0-3886	-0-0110	0-0022	„
„ 9(c)	0-2016	0-2005	0-2592	0-2136	+0-0120	0-0260	„
„ 10(c)	0-3008	0-1020	0-3316	0-3064	+0-0056	0-0135	„
„ 11(c)	0-2528	0-0572	0-2820	0-2542	+0-0014	0-0082	„
„ 12(c)	0-0546	0-2508	0-0652	0-0470	-0-0076	0-0046	„
EA 13(d)	0-1027	0-1012	0-1044	0-0992	-0-0035	0-0064	EFW
„ 14	0-1018	0-1012	0-1050	0-1000	-0-0018	0-0064	„

(a) By colorimetry.

(b) Hydrolysed with 75 c.c. HCl, not with HNO_3 .

(c) Quantities taken unknown to operator.

(d) Mixed earth acids.

An analysis of the figures obtained in these 14 experiments proves that Nos. 7 to 10 gave greater errors than the other 10 tests; in each of these four cases the weight of the oxide mixture was 0.4 gm. or more; hence our recommendation to work with small quantities, a point to which we return in the final paragraph of this paper. In the other ten tests, the results, whilst only approximate, are not erratic or grossly misleading. All the net earth-acid results (*i.e.* P^2 — TiO_2 in P^2) show a negative error; in other words, the amount of non-precipitated earth acid after double hydrolysis is greater than that of the co-precipitated titania.

CHECK TESTS CARRIED OUT IN THE U.S. BUREAU OF STANDARDS.—As on a previous occasion, Dr. G. E. F. Lundell and Mr. H. B. Knowles, of the Bureau of Standards, were kind enough to co-operate with us in this research by carrying out four separations by the nitric and tartaric hydrolysis method. In doing so, they worked with smaller quantities of the mixed oxides, thus obtaining a sufficiently close fractionation in one precipitation. In Exps. 1 and 2, the hydrolysis precipitate, P^1 , was next fused with potassium carbonate, and Muller's salicylic acid method applied; in Exps. 3 and 4, an additional step was introduced, in that the insoluble residue from the carbonate fusion was fused with bisulphate, the mass leached with salicylic acid, and this extract added to the solution of the carbonate melt, the combined liquors being boiled with excess of salicylic acid according to Muller. Either procedure gave a purified pentoxide precipitate P^2 , in which the remaining titania was determined colorimetrically, whilst the salicylic acid filtrate was added to the filtrate from P^3 . The main titanium filtrate (from P^1)—after destruction of the tartaric acid—was boiled with excess of ammonium

salicylate, which gave a small additional precipitate P^3 of earth acids not precipitated by the nitric-tartaric hydrolysis. The filtrate from P^3 , precipitated with ammonia, gave the bulk of the titania as P^4 . Table VII gives the results:

TABLE VII.

Exp.	Taken.	Weight. Composition.					Total. Products.	Error. Grm.
		P^1 . Grm.	P^2 . Grm.	P^2 . Grm.	P^3 . Grm.	P^4 . Grm.		
1.	TiO ₂	0.0307		0.0013(b)			0.0321	+0.0014
	M ₂ O ₅ (a)	0.0620	0.0606	0.0587	0.0574(c)	0.0025	0.0599	-0.0021
2.	TiO ₂	0.0325		0.0011(b)			0.0344	+0.0019
	M ₂ O ₅ (a)	0.0602	0.0599	0.0577	0.0566(c)	0.0018	0.0584	-0.0018
3.	TiO ₂	0.0295		0.0013(b)			0.0300	+0.0005
	M ₂ O ₅ (a)	0.0662	0.0668	0.0643	0.0630(c)	0.0023	0.0653	-0.0009
4.	TiO ₂	0.0295		0.0009(b)			0.0301	+0.0006
	M ₂ O ₅ (a)	0.0634	0.0620	0.0605	0.0596(c)	0.0027	0.0623	-0.0011

(a) Made up of equal parts of Ta₂O₅ and Nb₂O₅. (b) Determined colorimetrically.

(c) By difference.

It will be observed that in these tests the weight of P^1 agrees more closely with that of pentoxides taken than in our own analyses, in which larger amounts of earth acids were handled. The final error for titania is positive, that for pentoxide negative, in all cases. This, no doubt, is due to imperfect precipitation of the earth acids at the P^3 stage, a point requiring further investigation. Muller's method, both in its original form and in Lundell and Knowles' modification, gave a very incomplete extraction of the small amount of titania in P^1 in a single treatment (*cf.* our own tests under D, Part I). Writing of the method, Dr. Lundell states that in Exps. 3 and 4, the results were "most encouraging indeed."

ANALYTICAL APPLICATIONS.—The precipitation of the earth acids from tartrate solutions by nitric acid is useful not only as a separation from titania, but also from the common metals. It may therefore be applied to the tartaric acid solution of earth-acid minerals, as obtained in Schoeller and Powell's proposed process (Section I), where it may prove a very valuable adjunct. A closer study of the reaction is in contemplation; so far, zirconia in very large amount has been proved to interfere, in that it prevents flocculation and complete precipitation; tungstic acid, on the other hand, is precipitated along with the earth acids.

Although hydrolysis in tartaric solution has not, so far, given us quantitative figures, it precipitates the earth acids in a very much purer form than the customary hydrolysis of the pyrosulphate solution, in which there is pronounced contamination by adsorption of iron, manganese, etc. The process has already been applied successfully in actual practice in the analysis of tantalite, columbite, and a black sand consisting of columbite, cassiterite, ilmenite, and wolfram.

Finally, we wish to call attention to a development in the technique of earth-acid analysis which will be investigated and reported upon in due course. It is becoming increasingly apparent in the progress of this series of investigations that

the use of a large quantity of material does not lead to increased accuracy by reducing the relative error; on the contrary, the reactions involving the production of bulky or amorphous precipitates tend to proceed more smoothly and furnish better separations with less labour when the amount of material taken is reduced. This practice would constitute a slight approach towards micro-analytical work, the accuracy of which has been demonstrated in other branches of analysis. For the determination of the major constituents of earth-acid minerals the amount taken need not, we think, exceed 0.2 to 0.25 grm., a quantity with which a balance of a sensitiveness of 0.0001 grm. can adequately deal. This mode of working would also obviate another difficulty often encountered by the mineralogist, *viz.* collection of a sufficient amount of pure mineral for analysis.

SUMMARY.—The recent literature on the separation of titania from the earth acids is reviewed and criticised, to which end several processes were re-investigated. The following conclusions have been reached: (1) Hauser's mannitol method, which was apparently abandoned by its originator, is shown not to effect a separation. (2) The methods proposed by Weiss and Landecker were tested and criticised by a number of investigators, none of whom could reproduce a reliable separation. (3) Muller's potassium carbonate and salicylic acid process is relatively the best of the published methods. The very favourable results reported by him could not, however, be obtained; the earth-acid fractions obtained by the authors, although still titaniferous, gave consistently low recoveries. (4) Neither salicylic acid nor ammonium salicylate extracts titania from a pyrosulphate-hydrolysis precipitate, but titanitic acid precipitated by ammonia is soluble in either reagent; in the case of mixed earth acid and titania precipitates produced by ammonia, a more or less considerable proportion of the titania content is rendered soluble, but no quantitative separation was achieved. (5) Fusion of the mixed oxides with potassium carbonate and extraction of the mass with water is quite ineffective as a means of separation. (6) Volumetric methods for the simultaneous oxidimetric determination of titanium and niobium in presence of tantalum are too uncertain to serve as a substitute for actual separation.

A preliminary notice is given of the authors' proposed separation method, based on the dissociation of the soluble tartaric complexes of the metallic acids by a mineral acid; the earth acids are precipitated, the titanitic salt remains in solution. The results obtained are, as yet, only approximate; further work aiming at an exact separation is now in progress.

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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.

BULGING CANS OF LOGANBERRIES.

IN the August issue of *THE ANALYST* (p. 478) there is an abstract of the Annual Report of the Medical Officer of the City of London, in which attention is directed to a problem connected with the canned food industry.

It will be noticed that there is an apparent discrepancy between the reports of the City Bacteriologist and the Public Analyst, respectively, to the Medical Officer of Health. The Bacteriologist reported that the "blown" character of the tins could not be attributed to bacterial action (in the expression "bacterial action" he doubtless meant to include action by other micro-organisms, including yeasts), whilst the Analyst reported the presence of 0.20 per cent. of alcohol by weight, which he attributed to alcoholic fermentation. It is obvious from this, assuming that both reports are correct, that there was a difference in sample, and that some fermentation had occurred in the sample examined by the Analyst.

In view of the process adopted with these goods and the ease with which products of so high an acidity as loganberries are sterilised, it is obvious that if alcohol were actually present as a result of fermentation in the sample examined by the Analyst, the can was almost certainly a "leaker" or had leaked, at least, after processing. I assume, of course, that the Analyst made no error in his work, although the amount of alcohol reported was so slight that the results should be amply confirmed before a conclusion is drawn.

The gas pressure he reports and the bubbles rising to the surface after the can was opened might readily be accounted for by hydrogen, which always forms sooner or later when a product of this kind is canned, its formation, of course, being due to the action of the contents on the tin container. This hydrogen eventually forms in sufficient quantity to cause the ends of the can to bulge. In examining a product of this kind it is well to analyse the gas in the headspace, which is largely carbon dioxide when the swelling of the can is due to bacterial or yeast decomposition, but which is chiefly hydrogen when the swelling is due to hydrogen liberated by the chemical action of the contents of the tin.

The acid of the fruit is not the only constituent responsible for this attack on the container. It has long been known that oxygen in solution greatly accelerates corrosion, and the free oxygen which occurs to a considerable extent in apples may cause the bulging and also the perforation of a can. Moreover, the red soluble colouring matter of red fruits acts in the same way, since it contains oxygen, which, being in a very loose form of combination, acts as a depolariser.

It is surprising, at first thought, that cans protected with an inside lacquer are subject to more rapid corrosion, and hence to the more rapid bulging of the ends and perforation, than cans which are not so protected. This question is discussed by Kohman and Sanborn in a paper on "The Nature of Corrosion in Canned Fruits" (*Ind. Eng. J.*, 1924, 16, 290).

It is the soluble colouring matter of the fruit (together with the acid) that causes the difficulty, and the occurrence of pips, to which the Medical Officer refers,

is merely a coincidence. In fact, the same trouble is experienced with some varieties of cherries when they are packed in enamelled (lacquered) tins. Naturally, this chemical action of the fruit constituents on the cans is influenced by the temperature of storage.

Although the report of the City Bacteriologist is presented briefly, his results clearly indicate that the particular cans which he found were not sterile must have been "leakers," and the bacteria to which he refers must have entered the cans in that way. It has been found, almost without exception, that the bacteria which remain in the tin owing to insufficient heating for sterilisation are present as a pure culture. The occurrence of a mixed culture in a can of food (as in this instance) is almost certain evidence that a leak occurred through which the bacteria entered after processing. In practice, it is customary to find that whenever the sealing machine is not quite tight enough to close the can hermetically, the resulting leak is likely to admit bacteria, together with the water of the cooling tank, and then to become stopped up with particles of the contents of the can.

I have already written to the Medical Officer of the City of London, but, as the note published in *THE ANALYST* is likely to lead to misapprehension on the part of some of the English Health Officers and Public Analysts who have not given particular attention to the subject, I feel that the explanation of the difficulty given above may be of value.

W. D. BIGELOW.

THE NATIONAL CANNERS' ASSOCIATION,
WASHINGTON, U.S.A.

SODIUM FLAME FOR POLARIMETRIC WORK.

OWING to the difficulty of obtaining a sharp reading with coloured solutions in polarimetric determinations, we have used a sodium flame obtained by heating a pencil of the following composition:—Sodium chloride, 33; sodium bromide, 33; sodium silicate, 20; and magnesium oxide, 14 per cent. The sodium chloride, sodium bromide, and magnesium oxide are mixed with sufficient water to obtain a damp mass, and kneaded into the sodium silicate. The mixture is rolled out to about the size of an ordinary lead pencil, and dried in a water or air oven. The end of the pencil may be inserted in an ordinary Bunsen burner. If preferred, another 33 per cent. of sodium chloride may be substituted for the bromide, but the flame is not quite so brilliant.

T. MCLACHLAN.
A. W. MIDDLETON.

MESSRS. ALLEN & HANBURY, LTD.,
BETHNAL GREEN.

COMPOSITION OF A COUNTERFEIT COIN.

A COIN received in change from an unknown source in the Midlands proved to be a counterfeit half-crown. It had a bluish-grey colour and had evidently been reproduced by means of a mould from a genuine coin bearing the date 1924 and the mark of the Birmingham Mint. Though the impression was not sharp enough to bear close investigation, the whole appearance of the coin was sufficiently convincing for it to pass fairly easily, had it not been for the lightness which first led to its detection.

The coin was considerably under weight, weighing only 10.623 grms, as compared with 14.138 grms. (the weight of a new half-crown). The specific

gravity was 7.261, as compared with 10.346 for a genuine coin. It was composed of 97.33 per cent. of tin and 2.67 per cent. of copper, together with a trace of aluminium.

When the counterfeit coin and a genuine half-crown were placed in contact against the tongue, the galvanic effect was very marked—even more so than that produced by a copper and a silver coin in contact.

GEOFFREY C. MATTHEWS.

Notes from the Reports of Public Analysts.

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

CITY OF SALFORD.

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1926.

DURING the year, 3208 samples were analysed, 1387 being in connection with the Sale of Foods and Drugs Acts; of these, 62 (4.5 per cent.) were returned as adulterated. The total number of samples examined represents the purchase of 563 samples per 100,000 of the population.

MILK.—Of the 994 samples examined, 25 (2.5 per cent.) were adulterated. Two samples deficient in fat were found to be supplied by a farmer in another county. Section 8, sub-sec. 3 of the Milk and Dairies Consolidation Act, 1915, which came into force in September, 1925, was therefore put into operation, and the Inspector to the County of Chester was asked to take samples on behalf of the Salford Inspector. An “appeal to the cow” sample was taken and proved to be of good quality. Legal proceedings against the farmer were taken, and he was fined £3 and costs on each of the two samples.

Two samples taken on successive days at the station, after complaint, were found to be deficient by 10 per cent. in fat, whereas samples taken from two other churns of the same farmer’s milk were genuine. It was subsequently found that each time samples were taken the difference between the fat content of the morning milk and the evening milk was abnormally great (0.7 per cent.). Enquiry of the farmer showed that there was a difference of 10¼ hours between the morning and afternoon milkings, and 13¾ hours between the afternoon and morning milkings, and he was advised that by making the intervals more equal the quality of the milk from the morning milking would be improved.

CHEESE.—Five samples of Cheshire cheese, containing from 34 to 42 per cent. of fat, were returned as genuine. It is interesting to note that the Cheshire Farmers’ Union has lately adopted a standard of 45 per cent., calculated on the dry cheese, for genuine Cheshire cheese, and that the Cheshire Cheese Federation is establishing a registration scheme and a trade mark, with the aim of assuring customers that cheese bearing the trade mark will be genuine Cheshire cheese, produced under clean conditions.

TOFFEE.—An informal and a formal sample were examined of a toffee which was described as follows:—“The wonderful melts-in-the-mouth flavour is the

direct result of using only those ingredients which should go to the making of the best toffee—eggs, butter, cream, milk and sugar.” The percentage of protein showed that eggs, butter, cream and milk, if present at all, were present in extremely small quantities. In addition, the toffee contained 35 per cent. of glucose syrup. Correspondence with the manufacturers of the toffee was followed by the discontinuance of the advertisement.

COD-LIVER OIL AND MALT EXTRACT.—Three samples sold under a proprietary name were examined. The original description and advertisement stated that “the vitamin qualities are fully retained,” and that the oil was “robbed of its oily taste and fishy smell” and “all its wonderful qualities retained and reinforced.” It was also definitely stated that it *contained* cod-liver oil. Examination showed that it did not contain unchanged cod-liver oil, but about 30 per cent. of hardened and deodorised oil.

A series of feeding experiments, made by a well-known investigator, showed that both vitamin *A* and vitamin *D* were present, and that although the preparation was not equivalent in value to ordinary untreated cod-liver oil, yet it was about twice as rich as an average sample of butter in these factors. In view of these facts and of the much more guarded statements now made in the advertisements, the matter was not carried further.

BEEF AND MALT WINE.—See the Reports (ANALYST, 1926, 51, 514 ; 1927, 80, 341).

CUSTARD POWDER.—One of three samples examined had statements on the packet, “Made from real eggs” and “Contains eggs.” Analysis showed that, at the outside, not more than 5 per cent. of egg was present. Correspondence with the manufacturers resulted in their substituting for the labels others in which no mention of egg was made.

MALTED MILK.—A preparation was sold to a large number of small shop-keepers by a traveller who in each case sold a box of 3 dozen packets for 4s. 6d., taking the precaution to collect his cash on the spot and to leave no address. The preparation contained over 50 per cent. of cane sugar, about 10 per cent. of starch, and a considerable amount of crude fibre. The material was, of course, unsaleable, and the shop-keepers have been warned and asked to communicate with the Health Committee if anything more is seen of the traveller.

STRENGTH OF SUNLIGHT TESTS.—An investigation was made during the year as to the comparative amounts of sunlight received at four different stations in Salford. The test consisted in exposing an acidified solution of potassium iodide contained in a small glass bottle, in the presence of air, and determining the amount of iodine liberated by the action of sunlight.

The following comparative results were thus obtained at the Regent Road station:—

Jan.	Feb.	Mar.	Apr.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.
37.4	55.1	128.2	98.9	225.0	199.9	245.8	219.3	198.8	127.3	43.5	34.5

The half-yearly totals for all the stations were as follows:—

	Regent Rd.	Nab Top. Sanatorium, Marple.	Ladywell Sanatorium.	Drinkwater Park.
1st half-year	744.5	885.8	842.9	876.9
2nd „	869.2	860.8	812.0	870.3

The effect of the comparative absence of dust and smoke in the air during the first half-year is striking. Whereas the totals for the outer stations are approximately the same for the two periods, the figure for the Regent Road station for the second period is about 16 per cent. higher than for the first period, showing

that the central area indirectly benefited by the coal stoppage, in that the amount of sunlight received during that period was much greater than it otherwise would have been. In the two months, July and September, the figures for Regent Road were actually higher than any of the others.

H. H. BAGNALL.

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.

ALLFOOD WITH RADIUM.*

ON or about July 28, 1926, the U.S. Attorney for the Southern District of California, acting upon a report by the Secretary of Agriculture, asked for the seizure and condemnation of five gross boxes of Allfood with radium, alleging that the article had been transported from the State of Colorado, and charging misbranding in violation of the U.S.A. Food and Drugs Act.

Analysis by the Bureau of Chemistry, U.S.A. Dept. of Agriculture, showed that the article consisted of about 86 per cent. of milk sugar and 14 per cent. of substances insoluble in water, comprising mainly talc and other mineral matter and a small amount of animal glandular tissue. Each tablet contained about 0.09 millimicrogm. of radium. Misbranding was alleged for the reason that the statements regarding the therapeutic effects of the article were false and fraudulent, since it contained no ingredient or combination of ingredients capable of producing the effects claimed; also for the reason that the name "Allfood with Radium" was misleading, in that the tablets were not all food, even without the radium. On January 17, 1927, a Californian firm appeared as claimant for the property, and the product having been re-labelled to comply with the law, the U.S.A. District Court for S. California ordered that the article should be released upon payment of the costs of the proceedings.

SACCHARIN IN GRAPE FLAVOUR.†

ON September 1, 1922, the U.S.A. Attorney for the Western District of N. Carolina, acting upon reports by the Secretary of Agriculture, asked for the seizure and condemnation of 100 lbs. of grape flavour, alleging that it had been shipped from the State of Georgia, and charging adulteration and misbranding in violation of the U.S.A. Food and Drugs Act.

Adulteration was alleged in that the article contained saccharin, in that it had been mixed and coloured in a manner whereby its inferiority was concealed, and in that it contained an added poisonous or deleterious ingredient, saccharin, which rendered it injurious to health. Misbranding was alleged in that the article was labelled with the intent of deceiving the public, and in that it was offered for sale under the distinctive name of another article.

On October 11, 1926, no claimant having appeared for the property, judgment of condemnation and forfeiture was entered, and the Court ordered the product to be destroyed by the United States Marshal.

* U.S.A. Dept. of Agriculture, Bureau of Chemistry. 1927. Supplement. No. 14,832.

† *loc. cit.*, No. 14,845.

Report of the Government Chemist upon the Work of the Government Laboratory.

FOR THE YEAR ENDING MARCH 31ST, 1927.*

THE Report is on the same lines as in previous years (ANALYST, 1926, 51, 517-519). The total number of samples examined, including those at the chemical stations was 469,642, an increase of 24,036 over 1925-6. The samples of wine increased, those of tea decreased, chiefly owing to examination by trained tea inspectors, who send special samples only to the Laboratory. Exported tobacco and snuff samples increased, showing a maintained increase in exports. The silk duties involved the examination of over 22,000 samples, and the Safeguarding of Industries Act 10,000.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter*.—Only 3 out of 847 samples of butter and 4 out of 341 of margarine contained excess of water. One sample of butter from a home factory contained vegetable oil, and 3 out of 21 margarines contained excess of water.

Cheese.—One hundred and twenty-three samples were examined; 57 per cent. had been prepared from whole milk, 19 from milk containing three-fourths to the whole of its fat; 9 from milk containing half to three-quarters, and 15 from milk containing a third to a half of its fat.

Cream.—If more than 35 per cent. of fat is present, hydrogen peroxide or boron preservative not exceeding 0.4 per cent. may be added if the receptacle is labelled "preserved cream." The 25 samples of preserved cream examined contained 47-52 per cent. of fat, and the 80 unpreserved creams 20-33 per cent., with the exception of 2 samples containing 50 per cent.

Condensed Milk.—Of 153 samples, 43 were reported against, mostly for offences connected with labelling, but in 5 cases the milk was below the minimum standard.

Sheep Dips.—Eighteen of 118 samples were reported defective.

Water and Pollution of Rivers.—Thirty-six samples of river water and effluents were examined, and the salinity of 4385 samples of sea water taken, in addition to those examined for the Admiralty.

Fertilisers and Feedings Stuffs Act.—The new Act is not yet in force. Two fertilisers reported on consisted of a mangold manure deficient in potash and a blood and bone fertiliser. Of 8 feeding stuffs, 3 samples of barley meal contained 33-40 per cent. wheat offals, maize meal or mixed cereal meal, and one a large proportion of barley offal. A fattening meal was deficient in protein; a fish meal had an excess of oil and deficiency of protein, and a Sussex ground oats 20 per cent. of tapioca meal and 15 per cent. wheat and barley. No cases of disagreement with the results of the agricultural analysts were found.

Merchandise Marks Act.—Two of 12 samples of honey were incorrectly described as "Heather Honey" (*cf.* ANALYST, 1927, 340).

Miscellaneous Articles.—Eighty-eight samples examined included 2 samples of barley, one with a large proportion of weed seeds and about 15 per cent. of ill-developed oats, and another from N. Africa, which had peculiarly long and thin

* Obtainable at Adastral House, Kingsway, W.C.2. Price 1s. 3d. net.

grains with long awns, and showed a high proportion of fibre. A sample of sea sand used as a fertiliser contained over 50 per cent. of calcium carbonate.

Arsenic in Apples.—Four batches of apples were examined for insecticide remaining after spraying, but the quantity of arsenic found never reached the limit generally accepted as undesirable in food stuffs.

The Committee on the Method of Estimation of Fibre in Feeding Stuff has reported on a proposed method to the Advisory Committee preparing regulations under the new Act, and to the Ministry.

AIR MINISTRY.—Samples examined numbered 778.

CUSTOMS AND EXCISE.—*Beer.*—The total number of samples examined, mostly for original gravity, was 56,725, an increase of 1198 over the previous year. Of these, 233 were malt, corn, brewing sugars or spent grain, and 251 were yeast foods and other substances used in the preparation of beer; 7243 samples of wort or beer, of which the original gravity was declared by the brewers at a figure between 1 and 5 degrees too low in 235 cases, and more than 5 degrees low in 2 cases; 2860 samples of spoilt beer; 6562 samples for checking dilution, in 32 of which dilution equivalent to over 4 gallons of water per barrel was found; 89 samples of non-alcoholic beer, herb beer and beer substitutes, in 20 of which proof spirit exceeded 2 per cent. and in 14 from 2–6 per cent.; only 66 out of 19,475 samples of beer examined for drawback were over-declared; imported beer other than that from the Irish Free State has decreased in quantity, and only 3070 samples were examined, as compared with 10,000 in 1913–14, but 15,196 samples from the Free State were recorded; 53 out of 1805 samples tested for arsenic slightly exceeded the limit.

Cocoa and Chocolate.—Of 14,972 samples examined for duty, 11,011 were from imported, and 3961 from exported goods, and 4503 of the imported samples were examined for spirit.

Dangerous Drugs Act.—None out of the 54 samples contravened the regulations.

Silk.—In connection with duty 22,179 samples were examined, 1276 from imports, 9231 from exports, and 188 from home factories.

Duty-free Spirits.—The largest number of samples was under the heading “exported spirituous preparations,” and in 191 cases out of 17,846 the declared strength was over-estimated.

Sugar, Glucose and Saccharin.—Articles containing sugar or other sweetening matter analysed for duty purposes were 57,346, and included many miscellaneous articles, such as meat extracts, sauces, glue, etc. Saccharin was searched for in 376 imported samples, and in 363 samples for export, and 63 samples of saccharin and of materials used in its production were taken from home factories. Of beet pulp, juice, molasses, etc., 3994 samples were examined for subsidy purposes.

Tea.—Out of a total of 34,957 samples, 680 were reported against, representing 12,619 packages of tea.

Tobacco.—Moisture (limited to 32 per cent.) was determined in 9358, and oil (limited to 4 per cent.) in 1346 samples for home consumption; 16,523 samples were examined for drawback for export. Of offals, 2885 samples of stalks for drawback, 7959 for uniformity of condition and 7864 samples of offal snuff, shorts, etc., were examined.

HOME OFFICE.—Eighty-five samples were submitted by the police, and 13 of medical preparations by the Home Office. A sample of putty powder contained 53 per cent. of lead monoxide.

SALE OF FOOD AND DRUGS ACT.—Samples referred by magistrates were 45; 29 milks, 5 butters, 3 jams, 1 each of baking powder, cream, gin, mustard, sausages, shredded suet, whisky and wine, and in 36 cases results were in agreement, and in 8 in disagreement with those put forward by the prosecution. The latter were as follows:—Three samples of butter alleged to contain foreign fat were found to afford no chemical or physical indications of adulteration, and their characteristics were consistent with the samples being genuine butter containing a low proportion of volatile acids; 3 samples of milk alleged to be deficient in fat contained respectively 3·02, 3·07 and 3·35 per cent. of fat; a sample of baking powder was found to contain 4·8 per cent. of available carbonic acid, which did not support the allegation that it was useless as baking powder; a sample of shredded suet alleged to contain an excess of rice flour contained 15·51 per cent. of dry rice flour and 1·33 per cent. of moisture; and a sample of mustard alleged to contain wheat flour and turmeric was found to contain turmeric, but only a trace of wheat.

D. G. H.

Department of Scientific and Industrial Research.

REPORT OF THE STONE PRESERVATION COMMITTEE.*

WORK already done on stone preservation shows the importance of the micro-structure of the stone, particularly the distribution of pores. It is now possible to determine the bacterial content of different kinds of stone and it has been found that micro-organisms are present in stone of a quarry to a depth of 2 ft. below the face, so that investigations of anaerobic bacterial activity may be as important as, or more so, than those of aerobic activity, although it is not yet possible to say whether bacteria play an important part in stone decay. Stone flora are limited to a small number of species, and so far 12 have been isolated. A series of 14 piers of each of 6 kinds of stone, 7 with dished and 7 with weathered tops, has been erected, one specimen of each kind being left untreated and the remainder treated with preservatives of representative types. The first treatment was given in the summer of 1926 and a periodic inspection is intended.

APPENDIX I. REPORT ON EXPERIMENTAL INVESTIGATIONS, MAY, 1923— JUNE, 1925. (SCOTT RUSSELL.)

PREPARATION OF THIN SECTIONS OF FRIABLE MATERIALS.—These were most satisfactorily made by impregnating the specimens at ordinary temperature with the synthetic resin "bakelite," which is then converted into an infusible solid without appreciable volume change. Phenol and formaldehyde in roughly equimolecular proportions are heated with a suitable catalyst, a mobile aqueous liquid and a viscous resinous one being formed. The latter is separated, dehydrated *in vacuo* at 30–40° C., until the refractive index reaches about 1·59, heated with or without pressure, so that, passing through the fusible solid stage, it becomes infusible at a temperature below charring point (300° C.), and forms a clear yellow glass-like substance. The synthetic resins are in themselves extremely non-reactive with any ordinary minerals and are stable except to caustic alkalis, which are never found in the stones under investigation, and no appearance of distortion has been observed in any specimens prepared by the impregnation method. Resins

* Obtainable at Adastral House, Kingsway, W.C. 2. Price 1s. 3d. net.

produced by the condensation of formaldehyde with carbamide and similar substances are not suitable for impregnation, owing to their forming jellies at an early stage in the condensation. Products of formaldehyde with phenols and cresols, or both, are suitable, but condensation must be carried to a certain minimum degree *in vacuo*, or the final resin will not be clear. If carried too far, permeation will be slow and risk of mechanical distortion increased. By continuing the dehydration carried to a refractive index of 1.59 at 15° C. on the Abbé refractometer the formation of a clear resin is ensured. Addition of *m*-cresol to phenol-formaldehyde resins increases the rate of condensation and hardness of the residue and decreases the colour. Too little formaldehyde yields a resin which never hardens completely, and excess of formaldehyde produces a series of circular flat cracks in the final resin. The cyanide method of Romijn (*Z. anal. Chem.*, 1897, 36, 18) for determining formaldehyde is unaffected by the presence of phenol. Clear resins free from cracks gave values of 15–20 per cent. for free phenol, and 5 consecutive determinations gave, on one sample of resin, 16.2, 18.1, 17.4, 18.3, and 19.1 per cent. of phenol.

THE MECHANISM OF WEATHERING.—Material is lost from exposed stone surfaces either in solution by rain water or, what is more destructive, as solids, and intimately connected with this loss is the microstructure of the stone. Data as to porosity, density, etc., are only useful if accurately correlated with information as to the distribution of pore spaces and of the different chemical constituents.

POROSITY AND WEATHERING.—In the sections, as impregnated, pore spaces are filled with liquid resin which in the last stage of condensation passes into an infusible solid, so that if a section of an impregnated limestone is cut and treated with dilute acetic acid, the cast in resin of the pore spaces is obtained and may be mounted in a glycerin jelly of high ref. index (1.459^{15°}). By this means important differences in Portland stones have been found, and the examination of other stones is contemplated.

STRUCTURE OF THE WEATHERED SURFACES OF VARIOUS BUILDING STONES.—Sections of weathered Portland, Bath, Caen and Gatton stones and Elgin sandstone have been cut. Portland stone exposed to London atmosphere showed the removal of calcite from one part of the stone, deposition of gypsum in the pores, and re-deposition, on sheltered surfaces, of calcite which had persisted as a surface skin. This would be expected if the crystals were larger than the original ones. In soot-coated areas the outer black layer consists largely of soot and dust cemented together by well crystallised gypsum, and behind this is a well defined layer of gypsum, free from soot and dust. Calcium sulphate filled the macro pores to an average depth of 10–15 mm. Sulphuric acid may convert calcium carbonate directly into gypsum (as found on a heavily sooted stone from Somerset House) without the latter going into solution. Solution may be brought about by concentrated (owing to evaporation) rain water, but for direct conversion a soot layer seems to be essential.

PRESERVATIVES FOR THE TEST PIERS.—The following preservatives have been tested in the laboratory by a modification of Laurie's method (*J. Soc. Chem. Ind.*, 1925, 44, 86T), whereby pieces of treated stone were exposed in a closed vessel at ordinary temperature to fumes from a solution of hydrochloric acid:—(1) *Paraffin wax* in a solvent, of which ligroin and low melting point waxes were found the most satisfactory. (2) *Sodium silicate.*—Precipitation of barium silicate is better than precipitation of silica, and baryta is a more efficacious precipitant than barium chloride. The initial protective power of sodium silicate alone increases with the concentration of the solution used, and removal of by-products

of reaction ensures better results. (3) *Baryta*.—Barium arsenate was found as effective as barium silicate or barium sulphate as a protection against acid fumes.

Aluminium sulphate gives better results in other methods of precipitation than sodium or magnesium sulphate, probably because aluminium hydroxide is insoluble and helps to fill the pores of the stone. In general, aluminium sulphate is better than magnesium sulphate, sodium sulphate, or hydrofluosilicic acid; for precipitation of barium arsenate arsenic acid is better than sodium arsenate; barium arsenate fills the pores as well as barium sulphate, and no advantage results from precipitating the insoluble substances as colloids. In order to determine the depth to which the preservative penetrates, treated specimens of stones are being impregnated with bakelite and sections cut.

D. G. H.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Determination of Milk Fat in Milk Chocolate by means of a Modified Xylene Number. C. A. Greenleaf. (*J. Assoc. Off. Agric. Chem.*, 1927, 10, 396-404.)—The following procedure is recommended for the determination of a modified xylene number for fats:—Ten grms. of the fat are saponified gently over a small flame in a tared 500 c.c. Erlenmeyer flask with 20 c.c. of a mixture of 300 c.c. of glycerol with 80 c.c. of a solution containing 750 grms. of potassium hydroxide per litre. When perfectly clear, the liquid is mixed with 175 c.c. of hot, recently boiled distilled water and, when the temperature has been brought to 80° C. in a water-bath, with 51 c.c. (measured at 80° C.) of a solution containing 150 grms. of magnesium sulphate per litre, this being added gradually and the flask whirled meanwhile. The flask is cooled to 20° C., and its contents made up to 260 grms. with distilled water at 20° C. The stoppered flask is shaken vigorously and immersed for 5 minutes in a water-bath at 20° C. The liquid is then filtered through a Buchner funnel with the aid of suction, the magnesium soaps being pressed and thoroughly drained. Two hundred c.c. of the filtrate are shaken vigorously, at intervals of 5 minutes, in a separating funnel, with 50 c.c. of sulphuric acid solution containing 17 grms. of the concentrated acid per 500 c.c. and 50 c.c. of xylene. When the layers are separated, the aqueous layer is filtered through a pleated filter, and 200 c.c. of the filtrate mixed with 50 c.c. of water in a 500 c.c. Florence flask. After addition of pumice, the liquid is distilled, and exactly 200 c.c. of distillate collected in about 40 minutes, use being made of the Polenske apparatus. The distillate is titrated with 0.05*N* alkali in presence of phenolphthalein, the result being corrected in accordance with that of a blank test carried out similarly but without fat, and then divided by two to give the xylene number. This represents the number of c.c. of 0.1 *N* alkali required to neutralise the volatile fatty acids which are obtained from 6.4 grms. of the fat and are neither precipitated as insoluble salts by magnesium sulphate nor extracted from an acidified aqueous solution by 20 per cent. of its volume of xylene.

Twelve samples of butter fat gave xylene numbers ranging from 25.2 to 27.5 (mean 26.18), and six samples of cacao butter values of 0.10 to 0.40 (mean 0.19). The percentage of butterfat in a mixture with cacao butter is given by the expression (xylene number, 0.19) \div 0.288, if the xylene number is less than 11.72; or by (xylene number—2.08) \div 0.241, if the xylene number is greater than 11.72.

In applying this method to the examination of milk chocolate, the weight of sample that must be extracted to yield the required quantity of mixed fat can be calculated from the percentage of total fat, F. The percentage of milk fat in the entire sample is then given by $(F \times P)/100$, where P is the percentage of milk fat in the extracted fat.

T. H. P.

Determination of Added Disodium Phosphate in Process Cheese.

I. M. Williams. (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 302–307.)—Process cheese is mostly made with the aid of emulsifiers, disodium phosphate being the cheapest and commonest of these. Determinations of the phosphoric acid and lime give for the maximum, minimum and mean values of the ratio $P_2O_5:CaO$ the following results: For 28 samples of American cheese, 1.210, 1.023 and 1.094 respectively; for 11 of Swiss cheese, 1.214, 0.999 and 1.043; for 12 of brick cheese, 1.161, 1.030 and 1.096; for 7 of process American cheese with no added disodium phosphate, 1.114, 1.058 and 1.076; and for 8 of process American cheese with added disodium phosphate, 1.964, 1.400 and 1.662. The added disodium phosphate (as P_2O_5) is given by $X-YZ$, where X and Y are the phosphoric acid and calcium oxide present, and Z is the average value of the $P_2O_5:CaO$ ratio for the kind of cheese under examination.

T. H. P.

Behaviour of the Anthocyanin Pigments in Canning. **C. W. Culpepper.**

(*J. Agric. Res.*, 1927, **35**, 107–129.)—The pigmented portions of fruit and vegetables containing anthocyanin pigments are liable to violet, pink or purple discolorations when canned in tins (plain or enamelled) and the discoloration, which is due to complex violet metallic compounds of anthocyanin, is intensified on exposure to air. The anthocyanin of the peach has been isolated and partly purified, and the behaviour of many anthocyanin-containing fruits and a few vegetables, including peaches, plums, sweet and sour cherries, apples, red and black raspberries, blackberries, currants, grapes, mulberries, berries of *Viburnum* and *Crataegus*, red cabbage and beets, has been studied by canning tests in glass and plain and enamelled tin, as well as the comparative behaviour of aqueous solutions of the pigments with metals. The amount of the violet compound formed between the red anthocyanin pigments and the tin or tin salts (formed by combination of the fruit acids with the tin) depends on the amount of pigment present and degree of acidity of the medium, low acidity favouring the formation. The colour changes are reversible; addition of alkali to the solution of pigment containing metal results in a more intense coloration, and addition of acid destroys the combination and violet colour, and restores the original red. Since the pigment takes the metal from the metal salts, the fruit acid is released and can go on attacking the

tin, so that with low initial acidity favouring formation of metal salts, extensive attack will occur up to the limit of the metal-absorbing capacity of the pigment, but with high acidity formation of the metallic anthocyanin compound is reduced, solution of the metal being limited to the absorbing capacity of the acids present and equilibrium is reached before extensive corrosion occurs. Enamel preserves the original colour of red fruits and decreases contact between pigment and metal, but it increases the rapidity with which perforations occur, by limiting the area from which metal can be removed. Anthocyanin is important in causation of corrosion and perforation, but these processes can also be brought about by other means and are very complex.

D. G. H.

Characteristics of Cider. W. H. Bufton. (*J. Inst. Brew.*, 1927, **33**, 450-458.)—The three main groups of vintage cider apples are (1) sweet, (2) bitter-sweet, and (3) sour; (1) and (2) contain more sugar and give a juice of higher sp. gr. than (3), whilst (1) and (3) contain about the same average amounts of tannin, and (2) a greater proportion. (1) and (2) have less malic acid (0.2-0.3 per cent. than (3) (0.6-0.8 per cent.). It is not practicable to inoculate fresh apple juice, natural yeasts almost invariably becoming dominant over even heavy additions of pure yeasts. Washing of the fruit helps to keep down acetic fermentation, and the *apiculatus* type of yeast appears to be more readily washed off than *S. cerevisiae*. The freshly expressed apple juice has a sp. gr. of 1.044 to 1.056, occasionally even 1.060. The sugars consist of cane sugar (0.25 of the total sugar), dextrose (not over 0.2 of total sugar) and laevulose (seldom less than 60 per cent., rising to 90 per cent. of the total), the total sugar in apple juice being generally between 10 and 14 per cent. The tannin of apple juice (0.5-0.3 per cent. for sweet and sour, and up to 0.3-0.6 for bitter-sweet fruit) differs from gallotannin, and appears to be more closely allied to that of catechu and coffee, giving a reddish brown colour with caustic alkalis and precipitating vegetable albumins and gelatin. Clean sound apples only contain an average of 0.01 per cent. of nitrogen (Warcollier, *Cidrierie et Pomologie*), and only half is assimilable by yeasts. Fermentation starts about 3-4 days after pressing, and in 14 days the sp. gr. will have fallen to 1.025-1.030, when a first filtration is made to retard the process. The total acetic acid in cider should not exceed 0.075 per cent., and with the best ciders should be between 0.03 and 0.05 per cent. Less than 0.2 per cent. of malic acid renders the cider liable to sickness, especially if the sp. gr. is high, and impairs flavour, but if over 0.5 or 0.6 per cent. is present long storage will be necessary to prevent a harsh flavour. Total sulphurous acid must not exceed 200 parts per million (*Preservatives in Food Regulations*), and the use of sulphured casks should be avoided, as the sulphurous acid content of the cider may thereby be doubled.

D. G. H.

Volatile Alkaloid of Pepper. A. Pictet and R. Pictet. (*Helv. Chim. Acta*, 1927, **10**, 593-595.)—The alkaloid which accompanies piperine in black pepper and is volatile in a current of steam (*cf.* Pictet and Court, *Ber.*, 1907, **40**, 3776) yields 3-methylpyrrolidine when reduced by means of tin and hydrochloric

acid, and is found to be one of the optically active modifications of 3-methylpyrroline. Its crystalline hydrochloride has $[\alpha]_D + 2.77^\circ$, and in aqueous solution decolorises permanganate rapidly in the cold and reddens when heated on the water-bath; with sodium nitrite it yields an oily nitrosamine which gives Liebermann's reaction, and when shaken with sodium carbonate and benzoyl chloride it forms an oily benzoyl derivative, insoluble in acids.

T. H. P.

Determination of Cocaine. E. O. Eaton. (*J. Assoc. Off. Agric. Chem.*, 1927, 10, 347-349.)—The results obtained in the examination of a mixture of lactose with 20 per cent. of cocaine hydrochloride by a number of analysts justify the recommendation of the following procedure as a tentative method for the determination of cocaine: A quantity of the sample representing about 0.2 grm. of the alkaloid is dissolved in 20 c.c. of cold water, the solution being treated with 2 drops of dilute hydrochloric acid, transferred to a separating funnel, rendered alkaline to litmus with fresh saturated sodium hydrogen carbonate solution, and shaken to exhaustion with petroleum spirit; four 20 c.c. portions of the spirit usually suffice. The combined solvents are filtered through a paper moistened with petroleum spirit, with which also the paper is washed. The filtrate is shaken vigorously in a separating funnel with a decided excess of 0.02 *N* sulphuric acid, which, together with two 10 c.c. portions of water used to wash the petroleum spirit, is titrated with 0.02 *N* alkali in presence of methyl red. Multiplication of the number of c.c. of 0.02 *N* acid used by 0.006793 gives the number of grms. of cocaine hydrochloride in the sample. A gravimetric method, which consists in weighing the benzoic acid formed on hydrolysis of the cocaine, is not so satisfactory, but, in conjunction with qualitative tests, furnishes an indication of the presence of cocaine.

T. H. P.

Biochemical, etc.

Iron Content of Animal Tissues. C. A. Elvehjem and W. H. Peterson. (*J. Biol. Chem.*, 1927, 74, 433-441.)—It is shown that by the use of either the Thomson method or the modified method suggested by Elvehjem and Hart (*J. Biol. Chem.*, 1926, 67, 43; *ANALYST*, 1926, 51, 258-259) for biological material high in phosphorus, the iron content of animal tissues may be determined accurately. Since the modified method is the longer of the two, it is advantageous to use the Thomson method whenever possible. In order to determine whether the modified method is necessary for the analysis, a means has been devised which consists in the measure of the recovery by the Thomson method of added iron. Analyses are given of thirteen beef tissues and twelve rabbit tissues. Tissues such as bone marrow, hide, intestines, heart and muscle are low in iron; tissues such as lung, spleen, liver and kidney are relatively high in iron. It was found that the modified method was required for seven of the beef tissues and five of the rabbit tissues, but it is impossible to generalise and give any definite percentage of phosphorus above which the Thomson method cannot be used. A number of analyses of spleen, liver and kidney taken from different animals are given. These

results may aid in the selection of liver high in iron for use in the treatment of anaemias. Calf spleen is more than twice as rich in iron as beef spleen, yet calf liver is lower than beef liver. Calf liver is low in iron, and prepared beef juice for infant-feeding contains only 11·8 per cent. of the iron in the original beef. Therefore some of the methods used to furnish infants with additional iron should be studied further.

P. H. P.

Gasometric Micro Method for Determination of Iodates and Sulphates and its Application to the Determination of Total Base in Blood Serum.

D. D. Van Slyke, A. Hiller and K. C. Berthelsen. (*J. Biol. Chem.*, 1927, **74**, 659–675.)—A rapid and precise gasometric micro determination of iodates, in the manometric apparatus of Van Slyke and Neill (*J. Biol. Chem.*, 1924, **61**, 527; Van Slyke, *J. Biol. Chem.*, 1927, **73**, 121) by the reaction— $2\text{NaIO}_3 + 3\text{N}_2\text{H}_4 = 2\text{NaI} + 6\text{H}_2\text{O} + 3\text{N}_2$, is described in detail. Sulphates are measured by gasometric determination of the iodate dissolved when the sulphate solution is brought into equilibrium with excess of solid barium iodate. This is classed as an insoluble salt, but barium sulphate is so much more insoluble that a double decomposition occurs, iodate going into solution and sulphate being precipitated. The reaction $\text{Ba}(\text{IO}_3)_2 + \text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{NaIO}_3 + \text{BaSO}_4$ does not go completely from left to right, but reaches an exactly reproducible equilibrium, fixed by the relative solubilities of barium sulphate and iodate. For determination of total base in serum, the serum is ignited with nitric and sulphuric acids, and the bases are converted into sulphates as described by Stadie and Ross (*J. Biol. Chem.*, 1925, **65**, 735). The SO_4 is then determined by the above procedure. The base from 0·16 c.c. of serum suffices for a determination, with an average error of 0·8 per cent. of the amount determined. Room temperature variations within ordinary limits can be disregarded in the use of the method.

P. H. P.

Determination of Adrenaline. **L. C. Baker and G. F. Marrian.** (*Biochem. J.*, 1927, **21**, 1005–1009.)—An adaptation of the colorimetric method of Folin, Cannon and Denis (*J. Biol. Chem.*, 1913, **13**, 477) for determinations on glands, to the small adrenal glands of about 0·03 grm. weight of the rat and pigeon, gave results of wider variation than was anticipated, and the rate of colour change of the adrenaline solution differed from that of the uric acid standard solution. The effect of such variable factors as temperature on the rate of colour production of solutions of adrenaline was accordingly studied, with the use of the glasses of a Lovibond tintometer as a standard against which to match the blue colour. The concentration of adrenaline does not affect the time of maximum colour development at any one temperature. The reaction velocity is greater at higher temperatures, the time taken to reach a maximum increasing as the temperature falls; at 25° C. the maximum is reached after 10 minutes, at 20° C. after 20 minutes, at 16° C. after about 35 minutes, and at 14° C. after about 45 minutes. The possibility of loss of adrenaline due to oxidation in the method of extraction employed by Folin, Cannon and Denis was also examined and found to be small, but definite. This loss takes place after the addition of sodium acetate to the hot

hydrochloric acid extract and was avoided by using cold trichloroacetic acid as the extracting agent. This acid proved satisfactory in every way and gave a clear protein-free filtrate. P. H. P.

Physiological Importance of Nickel. G. Bertrand and H. Nakamura. (*Compt. rend.*, 1927, 185, 321–324.)—Comparison experiments with mice to whose diet 0.0025 grm. of nickel chloride and 0.001 grm. of cobalt sulphate per kilo. of body weight were added, showed that, as a consequence, the mean duration of life had been prolonged from 19.7 days to 23.1 days. After death the organs were found to contain increased quantities of these metals, compared with those normally present. J. G.

Vitamins A and D of Spinach. S. G. Willimott and F. Wokes. (*Biochem. J.*, 1927, 21, 887–894.)—An acetone-ether extract of dried spring spinach has been prepared more than 200 times as concentrated as the fresh leaves. Tests showed it to be free from oxidising enzymes and to contain only about 1 per cent. of the mineral matter in the fresh leaves. A practically mineral-free extract could be administered to rats in large doses without upsetting the ratio of calcium to phosphorus. A few grms. of the extract were dissolved in petroleum spirit, decolorised with norite, filtered and evaporated, and a colourless, oily residue was obtained which gave transient blue colours with both arsenic trichloride and antimony trichloride, the test of Willimott and Wokes for vitamin A (*Lancet*, 1927, 2, 8). Takahashi *et al.* (*Inst. Phys. Chem. Res.*, Tokyo, 1925, 3, 81), with a vitamin A extract prepared both from cod-liver oil and from spinach, obtained transient blue colours with concentrated sulphuric acid, but this seems to be the first record of these colours, supposedly due to the vitamin, being obtained with the two above-mentioned reagents on a spinach extract. The extract was a potent and stable source of vitamin A, in that daily doses of 25 mgrms. secured complete freedom from xerophthalmia and induced satisfactory, though slightly sub-normal, growth in rats. The extract, when given to rats in doses supplying ample quantities of vitamin A, did not contain significant amounts of vitamin D—merely traces. However, the fact that vitamin D may be present in these small amounts, which can be greatly increased by exposure to the action of the same agent (ultra-violet light) and which under certain conditions appears to be responsible for the destruction of vitamin A, raises the interesting question of a possible balance between these two vitamins—a problem for further investigation. P. H. P.

Photochemical Production of Vitamin D from Ergosterol. O. Rosenheim and T. A. Webster. (*Lancet*, 1927, 213, 622–625.)—The lowest protective dose of vitamin D, induced by irradiation of ergosterol, is found to be $\frac{1}{10,000}$ to $\frac{1}{20,000}$ mgrm. per diem for the rat. Under the experimental conditions employed, the maximum activity is produced after 30 minutes by the radiations of the mercury-vapour lamp and remains constant on prolonged irradiation up to four hours. The amount of ergosterol disappearing during the reaction is not related to the amount of vitamin present at any given time during this period. It is suggested

that, after a short initial period, the formation and destruction of the vitamin proceed at the same rate, so that the activity remains constant till the available ergosterol is exhausted. The observation that ergosterol is activated by the radiations of sunlight, as well as by the long wave-length radiations of the mercury-vapour lamp, furnishes a cause for the curative effect of sunlight in cases of rickets.

T. H. P.

Activation of Sterol Fractions by Ultra-Violet Irradiation. **A. F. Hess and R. J. Anderson.** (*J. Biol. Chem.*, 1927, **74**, 651-657.)—Although cholesterol has been shown to develop antirachitic properties following irradiation with ultra-violet light, yet cholesterol purified by bromination fails to develop them. Recently Windaus and Hess (*Nachr. Ges. Wissensch. Goettingen*, 1927, 175; *Proc. Soc. Exp. Biol. and Med.*, 1927, **24**, 759), and Rosenheim and Webster (*Biochem. J.*, 1927, **21**, 127, 389; *ANALYST*, 1927, **52**, 424) have concluded that it is probably an allied sterol, ergosterol, which is removed in the course of bromination, and that this substance is the precursor of the antirachitic factor. Since cholesterol preparations obtained from various sources manifest differences in their physical properties, the authors have prepared some pure sterol fractions from maize oil to ascertain whether any of them would show antirachitic properties on irradiation. The top fractions, β - and γ -sitosterol, were much more stable and less soluble than the bottom fraction, α -sitosterol. The β and γ fractions could be kept for months in glass-stoppered bottles without showing change in colour or melting point, but the α -fractions, after a few weeks, acquired a yellow colour and a peculiar rancid odour. All three fractions were kept for about 1 year, then irradiated and tested on rats, and all were incapable of acquiring antirachitic properties, yet only the first two, β - and γ -, had been purified by bromination. Fresh preparations of α -, β - and γ -sitosterol were made from maize oil and again irradiated and tested, and α -sitosterol was found to be strongly antirachitic, whereas β - and γ -sitosterols were inactive. Therefore the substance capable of activation by ultra-violet light is present only in the α -sitosterol, the bottom fraction which has not been brominated. If it had been present in the less soluble portions, it was destroyed during bromination. Obviously, after standing for a year profound changes had been induced by spontaneous oxidation in the molecule of α -sitosterol. Whether traces of ergosterol, the so-called "provitamin," are present in maize oil is not yet known.

P. H. P.

The Effect of Waste Pimento Pepper on the Colour of Egg Yolks. **W. A. Morgan and J. G. Woodroof.** (*Georgia Expt. Station Bull.*, 1927, No. 147.)—Dried pimento pepper was added in varying known quantities to the feed of 10 hens, and 10 other hens were kept as controls. It was found that, regardless of the quantity of pepper given, the white of the egg was unchanged and the shell hardly affected, but that the yolk colour deepened in direct proportion to the amount of pepper given. Amounts of pepper ranging from 0.3 to 0.5 gm. per hen per day produced yolks of varying shades of yellow, 0.75 gm. yellow yolks with a reddish tinge, and 1 gm. produced objectionably red-coloured yolks.

D. G. H.

Water Analysis.

Determination of Magnesia Hardness in Water. W. R. Atkin and D. Burton. (*J. Int. Soc. Leather Trades Chem.*, 1927, 11, 294.)—The usual method is employed, except that all titrations are carried out to an end point of P_H 3·7, brom-phenol blue being used as indicator. A standard solution for comparison is made by half-neutralising 0·1 *N* formic acid with sodium hydroxide solution. Two hundred c.c. of the water are titrated to P_H 3·7, boiled for 20 to 30 minutes to expel carbon dioxide and decrease the volume to about 70 c.c., cooled and transferred to a 200 c.c. graduated flask. Fifty c.c. of clear saturated lime-water are added, and the flask heated in a water bath to boiling temperature. It is cooled, its contents diluted to 200 c.c. with water free from carbon dioxide, carefully mixed (not shaken), and left till clear. One hundred c.c. of the clear solution are pipetted off and titrated to P_H 3·7 as before. The magnesia hardness, expressed as parts $CaCO_3$ per 100,000, is obtained by multiplying by 5 the difference between the first titration and twice the second titration. R. F. I.

Testing of Well-water for Pollution with Illuminating Gas. Regenstein. (*Chem. Zeit.*, 1927, 51, 737–738.)—In addition to hydrogen and methane, for which there are no definite reactions, well-water polluted by illuminating gas may contain the following impurities:—*Phenol*.—Bromine-water and Millon's reagent will detect 1·3 and 0·1 mgrm. per litre, respectively, if successive litre-portions of the water are extracted with ether after the addition of tartaric acid and 200 grms. of pure sodium chloride. This method is preferable to distillation for the removal of the phenol, but involves a loss by solution of 25 c.c. of ether per litre of sample. *Thiocyanates*.—Ferric chloride solution will detect not less than 0·1 mgrm. per litre. *Hydrocyanic acid*.—The Prussian blue test is applied to the first few drops of distillate from 1 litre of sample. A test solution prepared by bubbling gas into water gave no reactions for the three above impurities. *Oxygen absorption*.—Comparative tests at various temperatures showed that in 24 hours a much larger oxygen absorption was obtained at 45° C. than at 37° C. or at room-temperature. A solution of sodium thiosulphate was used for the back-titration, with a potassium iodide and starch indicator. The absorption due to the blank was relatively very small and independent of the time. *Chlorination*.—Various volumes of freshly-prepared 0·01 *N* chlorine water were added to 200 c.c. of sample in stoppered flasks, and the mixture well shaken and placed in the dark. The back-titration was done with sodium thiosulphate and a potassium iodide and starch indicator, and changed gradually with the time of standing. The smallest possible excess of chlorine water should be used, and the titrations continued till three successive readings agree. *Carbon monoxide*.—One litre of water is distilled into 15 c.c. of conductivity water cooled in ice. When the volume is 20 c.c., 1 c.c. of a 0·2 per cent. solution of palladium chloride is added, and the flask stoppered and allowed to stand in the dark for 24 to 48 hours. A black deposit denotes a positive reaction. This method is preferable to that in which the absorption

spectrum of defibrinated blood is observed in the presence of the distillate and of a solution of ammonium sulphide. *Acetylene*.—The sample (1 litre) is distilled into 2 c.c. of an ammoniacal cuprous salt solution prepared from 1 gm. of crystalline cupric sulphate, 4 grms. of ammonium hydroxide (20 per cent. NH_3), and 3 grms. of hydroxylamine hydrochloride, in 50 c.c. of water. The reagent keeps for less than a day in the dark and must be cooled in ice. The adapter from the condenser should dip directly into the reagent, and the boiling of the sample should be regulated so that the first bubbles of gas enter the reagent slowly. Less than 4 c.c. of distillate are collected, and a red colour, followed by a red precipitate after a time, denotes a positive reaction. J. G.

Bacteriological.

Production of Acetylmethyl Carbinol by *Clostridium Acetobutylicum*.

P. W. Wilson, W. H. Peterson and E. B. Fred. (*J. Biol. Chem.*, 1927, 74, 495–507.)—In a previous paper by McCoy, Fred, Peterson and Hastings (*J. Infect. Dis.*, 1926, 39, 457) it was reported that qualitative tests showed the production of acetylmethyl carbinol ($\text{CH}_3\text{CHOH.CO.CH}_3$) from more than twenty different carbohydrates by the acetone-butyl alcohol-producing organism *Clostridium acetobutylicum* (Weizmann). The production of this compound at various stages during the fermentation has been studied quantitatively in order to determine the factors which accelerate or retard its development and to gain an insight into the general mechanism of the fermentation. It is shown that acetylmethyl carbinol is produced in the butyl alcohol fermentation as a regular end-product, as the quantity present increases throughout the fermentation. The amounts formed average from 300 to 400 mgrms. per litre and appear to have a fairly definite limit. Acetylmethyl carbinol is formed at about the same time as the acids, acetic and butyric; probably all have a common precursor. The production of acetylmethyl carbinol is more closely connected with the formation of the acids than with solvent formation, and acetylmethyl carbinol is more sensitive to modifying factors than the solvents, acetone and butyl alcohol. The addition of phosphates increases the production of acetylmethyl carbinol, and the addition of large quantities of proteins decreases it and causes a rise in the acetone-solvent ratio. The addition of starch has practically no effect. Thus, only when external factors are changed sufficiently to modify the fermentation is the production of acetylmethyl carbinol affected. P. H. P.

Toxicological and Forensic.

Trichloracetates of the Alkaloids. Use of Trichloroacetic Acid in Toxicology. G. Florence. (*Bull. Soc. Chim.*, 1927, 41–42, 1097–1100.)—The Stas-Otto method, in which acid alcohol is used to coagulate albuminous matter and to extract alkaloids from tissues, is open to the objection that the alcohol also dissolves substances such as lipoids, lecithins and resins. These are difficult to

remove from the extract completely without loss of the alkaloid, and they may interfere subsequently with the colour reactions. Dragendorff's method avoids this objection by the use of sulphuric acid. Certain alkaloids, however, such as cocaine and atropine, are easily attacked by it at 60° to 70° C., and form decomposition products which cannot be identified. It is suggested that the alkaloids, etc., should be separated in the form of their trichloracetates, by adding them in equimolecular proportions to a hot aqueous solution of trichloroacetic acid. Those of aniline, the toluidines, strychnine, brucine, morphine, codeine, quinine, and quinidine form well-defined crystals. Those of cocaine, nicotine, atropine and cinchonine are amorphous masses, from the aqueous solutions of which the alkaloids may be obtained by the action of a solution of sodium bicarbonate. The salts are all soluble in alcohol or acetone, and insoluble in ether, benzene or ligroin. They are decomposed by boiling water into chloroform and carbon dioxide (from the trichloroacetic acid), and the base. J. G.

Agricultural.

Composition of New Zealand Bran and Pollard. L. D. Foster. (*N.Z.J. Agric.*, 1927, **35**, 19–22.)—The New Zealand wheat offals are separated only into bran and pollard, and not further subdivided into middlings, sharps, etc. The limits in composition for bran and pollards, as obtained from the analyses of 12 samples separated by an experimental mill, were:—Protein: bran, 16·25–10·41, pollards, 18·13–12·19; fibre, 11·63–9·67 and 5·92–3·42; ash, 6·12–4·20 and 4·14–2·57; oil, 4·65–3·00 and 4·87–3·87; carbohydrates, 58·07–52·66 and 64·41–56·42 per cent. D. G. H.

Organic Analysis.

Determination of Gallic Acid in the Absence of Tannin. M. Hirsch. (*Chem. Zeit.*, 1927, **51**, 718–719.)—To 20 c.c. of a boiling filtered 1 per cent. solution of gallic acid are added 10 c.c. of a filtered solution of bismuth nitrate reagent. This reagent contains 15 grms. of the pure crystalline salt dissolved in 30 c.c. of acetic acid, and diluted to 240 c.c. with water. The yellow precipitate of bismuth subgallate (dermatol) is allowed to settle while warm, filtered through a tared Gooch crucible, washed with hot water till free from nitric acid, and then with alcohol and ether. It is dried at 45° to 50° C. till it is constant in weight. Errors of from –0·5 to +0·9 per cent. are recorded for the determination of Merck's purest gallic acid. The method is to be preferred to the existing gravimetric methods, but cannot be used in the presence of tannin. J. G.

Salts of Linolenic Hexabromide. P. R. Almoradie. (*Philippine J. Sci.*, 1927, **33**, 257–263.)—The calcium, magnesium, strontium and nickel salts of crystallised linolenic hexabromide (from lumbang oil), have been prepared by converting the acid into the potassium salt, dissolving this in normal propyl alcohol, and treating the solution with an inorganic salt, such as calcium bromide,

dissolved in normal propyl alcohol. The salts were purified by washing with ethyl alcohol (50 per cent. and 95 per cent.), and dried *in vacuo*. They melted, incompletely and with decomposition, at temperatures varying from 208° to 218° C. With the exception of the potassium salt (which was soluble in hot normal propyl alcohol), all the salts were either insoluble or slightly soluble (1 per cent. or less) in the usual organic solvents.

Microchemistry of Coumarin. C. van Zijp. (*Pharm. Weekblad*, 1927, No. 34, 841-844.)—The botanical origin of coumarin is discussed, so far as concerns the plants *Eupatorium Lindleyanum*, *Ruta graveolens L.*, and *Artemisia dracuncululus L.* The fact that coumarin has been found by some workers but not by others in the last-named plant, is explained by the occurrence of two varieties of the plant, one of which contains coumarin, whilst the other does not. The principal physical properties of coumarin are also described, and, in addition to the iodine reaction of Senft and the thallium nitrate reaction of Behrens, a recent test, due to White, is described. A small single crystal of mercuric chloride is introduced into a small drop of a mixed solution of mercuric chloride and coumarin, and the formation of characteristic needle-shaped crystals is observed under the microscope. The author has improved this reaction by the addition of a small quantity of a colouring matter, such as Congo-red, to the solution. The formation of crystals on the edge of the solution is then more easily detected, particularly when it is otherwise obscured by the presence of other solid matter. J. G.

Method of Differentiating Vegetable and Animal Charcoals. S. Ahlbom. (*Apotheker-Zeit.*, 1927, 66, 969; *Pharm. J.*, 1927, 119, 298.)—Charcoal, starch and colophony, in the proportion of 2:1:1, are mixed, a finger print taken, and the fine mixture dusted over with a soft brush, the superfluous powder removed, and the glass heated for a few seconds over a non-blackening flame. A black fixed imprint, like an etching, is obtained with vegetable charcoals, but no fixation occurs with animal charcoals. D. G. H.

Inorganic Analysis.

Wulff Method of Determining the P_H value. C. E. Druart. (*J. Int. Soc. Leather Trades Chem.*, 1927, 11, 292.)—The principle of the method consists in immersing in the solution to be tested an absorbent material, containing the required indicator and enclosed in a membrane which allows H and OH ions to diffuse through it more rapidly than the indicator. The tint of the absorbent material is then compared with that obtained by immersing similarly prepared materials in a series of solutions of known P_H value. The time of immersion must be regulated so that the depth of tinting of the absorbent material is the same as the control; it varies from one to three minutes. By using Sørensen solutions accuracy to 0.05 P_H can be attained. The method has the advantage of being applicable to colloidal suspensions, and cloudy or coloured solutions. (No trouble

was experienced when experimenting with tan liquors to which methylene blue had been added.) The whole apparatus, with accessories, is conveniently packed in a case measuring 26 cm. \times 10 cm. \times 3 cm., and weighing 1 lb. R. F. I.

Determination of Sulphur Trioxide in the Presence of Sulphur Dioxide.

J. R. Eckmann. (*Scientific Papers of the Bureau of Standards, U.S.A.*, 1927, **22**, 277-285, No. 554.)—A brief review is given of the methods for the determination of sulphur trioxide in the presence of sulphur dioxide. The following method has been evolved and has been found preferable in connection with the study of the heat of formation of sulphur dioxide. A solution of barium sulphite (prepared by saturating a 1 per cent. solution of crystalline barium chloride in 0.02 *N* hydrochloric acid with sulphur dioxide) is forced by means of a stream of nitrogen into a reaction vessel. A measured sample of gas is then bubbled through the reagent, and the precipitated barium sulphate separated on a sintered glass filter-plate and washed with oxygen-free distilled water. The whole series of operations is carried out in a closed apparatus from which all oxygen has been expelled by means of a stream of purified nitrogen, and oxidation of the barium sulphite is thus avoided. The precipitate is then washed into a weighed platinum dish, the last traces removed from the apparatus in boiling 2 *N* hydrochloric acid, added to the bulk, and evaporated in the presence of sulphuric acid in the usual way. A blank experiment gave a result of 0.0001 grm. of sulphur trioxide, and the error on an added amount of sulphur trioxide (0.0412 grm.) was -0.0002 grm. The filtering device removes the sulphur trioxide completely, but one which enables an ordinary filter-paper to be used is also described. Filtration is assisted by suction, but the liquid is replaced by nitrogen during its removal. The gaseous portions of purified and commercial samples of sulphur dioxide were found to be free from sulphur trioxide, but the residues contained from a trace to 0.0032 per cent. J. G.

Volumetric Separation of Selenium and Tellurium. L. Moser.

(*Chem. Zeit.*, 1927, **51**, 729.)—The method for the volumetric separation of selenium and tellurium suggested by Littmann (*ANALYST*, 1927, 365) is criticised. In particular, it is pointed out that the oxidation of tellurium dioxide by potassium dichromate in the presence of sulphuric acid is slow and not quantitative. It is preferable to dilute the solution of tellurium dioxide in hydrochloric acid with water, and to add a solution of sodium hydroxide till a slight turbidity appears. A known excess of 0.1 *N* potassium dichromate solution is then added, and after it has stood 10 minutes on the water-bath, the liquid is cooled quickly, and back-titrated with a solution of ferrous ammonium sulphate, made weakly acid with sulphuric acid. A fresh 1 per cent. solution of potassium ferricyanide is used as a spot indicator. The equation for the oxidation of tellurium dioxide by potassium permanganate is also questioned. Finally, the red selenium produced during the reduction of selenium dioxide by potassium iodide, adsorbs iodine continuously,

and produces what is either the compound SeI_4 , or, more probably, a mixture of solid phases. The method of Moser and Prinz is to be preferred (ANALYST, 1919, 44, 19, 61).
J. G.

Solubility of Cupric Sulphide in Alkali Sulphides in Presence of Sulpharsenates. C. Davies and A. D. Monro. (*J. Chem. Soc.*, 1927, 2385–2386.)—The solubility of cupric sulphide in a solution of yellow ammonium sulphide having approximately the composition $(\text{NH}_4)_2\text{S}_2$ increases steadily on addition of increasing amounts of arsenic until it becomes ten times its original value, so that it is possible for small amounts of copper in copper-arsenic mixtures to be missed in a qualitative analysis unless the arsenic group is examined for copper. When colourless ammonium sulphide is used in place of the yellow sulphide, no copper is found in the arsenic filtrate. Pure sodium sulphide gives irregular results, but a solution of sodium polysulphide of the composition Na_2S_2 gives stable solutions containing arsenic and copper.
T. H. P.

Sensitive Test for Bismuth. H. Kubina and J. Plichta. (*Z. anal. Chem.*, 1927, 17, 11–14.)—When a hot bismuth chloride or nitrate solution is treated with one per cent. dimethylglyoxime, and ammonia to strongly alkaline reaction, the whole of the bismuth is thrown down as an intensely yellow, very bulky precipitate. Sulphate solutions do not react, but the white precipitate turns yellow if sodium chloride is also added. The sensitiveness of the reaction is 1:70,420. The complex is decomposed by acetic acid; tartaric acid or its salts prevent the reaction.
W. R. S.

Volumetric Determination of Bismuth. W. Strecker and A. Herrmann. (*Z. anal. Chem.*, 1927, 72, 5–11.)—Three accurate methods were worked out. (1) *Phosphate Method.*—The nitrate solution (about 0.2 gm. Bi; 50 c.c.) is precipitated, while boiling, with 50 c.c. of 0.1 N disodium phosphate, added very gradually; when cold, the liquor is filtered into a graduated 500 c.c. flask, and the precipitate washed with water. The filtrate is treated with phenolphthalein and sodium hydroxide till just red, 50 c.c. each of sodium acetate and silver nitrate solutions (both 0.1 N) added, and the solution made up to volume. The excess of silver in 200 c.c. of filtrate is titrated according to Volhard. (2) *Oxychloride Method.*—The nitrate solution (25 c.c.) is treated with ammonia till cloudy, feebly acidified with hydrochloric acid, and heated to boiling, then drop by drop with strong hydrochloric acid till quite clear (1.5 to 2 c.c.), and 200 c.c. of hot water. The precipitate is collected and washed quite free from chloride, and dissolved in nitric acid. The chlorine in this solution is titrated according to Volhard. (3) *Permanganate Method.*—The nitrate solution (25 c.c.) is heated to boiling in a conical flask, the flame removed, 0.4 gm. of pure magnesium drillings added, and a Bunsen valve inserted. The flask is heated over a small flame for half-an-hour, when 40 c.c. of 2 N ammonium sulphate solution are added; heating is continued till the smell of ammonia has disappeared. The ammonium salt dissolves the

excess of magnesium. After cooling, the precipitated bismuth is collected and washed with boiled water, transferred to a small flask filled with carbon dioxide, and dissolved in 30 c.c. of ferric chloride solution (50 grms. FeCl_3 , 65 c.c. strong HCl, to 250 c.c.) by gentle warming. After cooling under carbon dioxide, the solution is rapidly filtered from the fragments of filter paper, which are washed with boiled water. The filtrate, after addition of manganous sulphate and phosphoric and sulphuric acids, is titrated with 0.1 *N* permanganate. 0.1 *N* equivalent weight for Bi=0.006933 gm. per c.c. (*cf.* ANALYST, 1927, 52, 250.)

W. R. S.

Rapid Determination of Nickel. G. Spacu and J. Dick. (*Z. anal. Chem.*, 1927, 71, 442-446.)—The solution (100 c.c.; 0.1 gm. Ni) containing 0.5 gm. of ammonium thiocyanate, is boiled, treated with one c.c. of pyridine, and stirred for a short time till the sky-blue crystalline precipitate appears. The cold solution is poured through a porous crucible; the precipitate is washed by suction 4 to 5 times with 35 per cent. alcohol containing pyridine and thiocyanate, twice with absolute alcohol containing pyridine, and finally 5 to 6 times with ether containing pyridine. After thorough suction, the crucible is left to dry at ordinary temperature *in vacuo*. Factor for Ni in $(\text{NiPy}_4(\text{CNS})_2)=0.1195$. The results cited are accurate. Manganese, cobalt, zinc, copper, cadmium, "etc.", interfere, and excess acid must be first removed by evaporation to dryness. (*Cf.* ANALYST, 1927, 430, 494.)

W. R. S.

Electrolytic Method for the Determination of Sodium and Potassium. J. L. Stoddard. (*J. Biol. Chem.*, 1927, 74, 677-688.)—A method is described which is designed for the determination of the sum of sodium and potassium, and thus of sodium by difference, if potassium is determined. The material is first ashed and dissolved, then magnesium and calcium are precipitated. Part of the remaining solution is electrolysed in a simple apparatus, which consists mainly of one test-tube fused inside another, with mercury in each tube, and a passage through the wall of the inner tube. Under an E.M.F. of 110 volts the negative ions migrate to the mercury in the outer tube. The positive ions migrate to the mercury in the inner tube, where they form an amalgam, which is then removed and titrated. Results agree within 2 per cent. when the quantity of sodium plus potassium is equal to at least one-fourth that contained in 1 c.c. of plasma. Directions for making the apparatus and for the method are given, together with some results obtained with known solutions. Experiments with additional negative ions showed only very slight deviations in the results, if any.

P. H. P.

Physical Methods, Apparatus, etc.

Physico-Chemical Analysis by means of the Boiling of Saturated Solutions. E. Cornec and P. Klug. (*Bull. Soc. Chim.*, 1927, 41-42, 1009-1017.)—The determinations of the b.pts. of saturated solutions for varying proportions of two constituent salts enable temperature-composition diagrams to be

obtained which indicate whether the salts combine, form a double salt, or form a continuous series of mixed crystals under these conditions. The solution is contained in a tube provided with a thermometer and stirrer, which is immersed in a thermostat of boiling tetrachlorethane, the temperature of which may be varied from 100° C. to 170° C. by corresponding variations in the pressure. The starting-point for each salt is the temperature at which crystals begin to separate from a boiling solution of the pure salt (the salt-temperature). It is given by the expression $(100 + t_1 - t_0)^\circ \text{C.}$, where $(t_1 - t_0)$ is the difference between the salt-temperature as determined from the time-temperature curve, and the b.pt. of pure water as read in the same apparatus and under the same conditions. Diagrams are shown to illustrate the application of the method to a number of salts. Mixtures of the chlorides of sodium and potassium, and also of their nitrates, behaved normally, *i.e.* the two branches of the curve met at a point which indicated the b.pt. of the solution when saturated with the two uncombined solid phases. The mixed chloride and bromide of sodium, and also of potassium, formed a series of mixed crystals, as was shown by a continuous curve. Copper and zinc sulphates each combined with ammonium sulphate to give the double salts $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, respectively. J. G.

Standard Samples. Dept. of Commerce U.S.A. Bureau of Standards, Bulletin No. 25.—The standard samples comprise analysed samples of various materials which may be used to check analyses of similar materials, so that a large number of variable factors may be investigated in the simplest manner and shortest time; and samples of fixed and definite chemical composition, such as standards for volumetric analysis, calibrating calorimetric bombs, etc., and metallic alloys. Details of the preparation of metals and alloys, ores and cements are given, and the following pure chemicals are issued:—*Sucrose* for calorimetric and saccharimetric standards is prepared from the purest commercial granulated sugar. *Dextrose*, as a standard reducing sugar, is prepared by dissolving the purest commercial dextrose in 40 per cent. of its weight of water, treating with decolorising carbon and filtering. Crystallisation is carried out in a rotating crystalliser, the crystals are centrifuged and washed with alcohol, and the process repeated until a satisfactory purity is obtained. The crystals contain 1 mol. of water of crystallisation, which is lost at 60° C., and remaining traces of water are removed by exposure to a temperature of 70° C. Although not very hygroscopic, the dried substance should be kept in a desiccator. The normal weight (that required to give a rotation on the quartz edge saccharimeter equivalent to 26 grms. of sucrose in 100 c.c.) is 32.231 grms., and the sp. rotation for wave length 5461A is represented by the formula

$$\left[\alpha \right]_{5461 \text{ A}}^{20.0 \text{ C.}} = 62.032 + 0.0422xp + 0.0001897 p^2$$

where p is the percentage by weight *in vacuo*. *Benzoic acid*.—The original sample was prepared from the purest synthetic acid obtainable, by two crystallisations from ethyl alcohol, and one crystallisation from water, followed by fractional

sublimation *in vacuo*, but if the raw material used contains 99.9 per cent. benzoic acid and is free from chlorine and sulphur compounds one crystallisation from water followed by the fractional sublimation is sufficient. Progress of purification is followed by titration with standard alkali. *Sodium oxalate* is also used as a standard sample. *Naphthalene* is prepared by two crystallisations from alcohol followed by sublimation *in vacuo*, and no attempt is made to obtain an absolutely pure product.

D. G. H.

References to Scientific Articles not Abstracted.

THE FILMS RESPONSIBLE FOR OXIDATION TINTS ON METALS. T. R. EVANS.
Nature, 1927, 120, 584 (Oct. 22).

Separation of the films from lead and from iron (*Proc. Roy. Soc.*, 1925, 107, A, 228; *J. Chem. Soc.*, 1927, 1020)—Physical differences—Lead oxide film transparent—Transparent, with minute opaque spots of metallic iron—Specific absorption of iron oxide films sufficient to mask colour due to interference.

THE TOBACCO HABIT. W. E. DIXON. *Brit. Med. J.*, 1927, 719–725 (Oct. 22).

Historical—Composition of the tobacco smoke—Carbonic oxide—Amount of nicotine in smoke—Denicotinised tobacco—Action of tobacco smoke—Specific action—Economical factors—Bibliography with 52 references. (*Cf. ANALYST*, 1926, 51, 319.)

Reviews.

THE MAKING OF A CHEMICAL. By E. J. LEWIS and G. KING. Pp. 280. London: Ernest Benn, Ltd. 1927. Price 12s. 6d. net.

In their introduction the authors state that this book is intended primarily for those entering the chemical industry, but they hope that it will find a wider use.

The whole of the first part of the book (88 pages) is devoted to the subject of cost, of which the average graduate leaving college is blissfully ignorant. Until the chemist learns to consider £ s. d. in every process connected with a works, he is likely to complain that the management do not appreciate his knowledge.

The authors lay particular stress on the efficiency of a chemist in analytical work, and warn the student not to allow his personal inclinations or desires to weight his results in order to make a case, since this "may overthrow even an experienced practitioner." Attention is drawn to the fact that a clear idea of the probability of error should always be kept in mind, as it is unnecessary to return figures to the second place of decimals, when the probability of error may be as great as 3 per cent. We read recently the analysis of a malt extract by a well-known chemist, in which all the constituents given were recorded to the second

place of decimals, making the total add up to 100 per cent., whereas even the qualitative analysis was incorrect.

The chemist is advised to make use of literature, both scientific and literary, and, in particular, of journals containing abstracts. In this connection a curious mistake is made on page 64, when referring to the *Journal of Biochemistry*; surely the authors mean *Physiological Abstracts*. Other errors are on p. 32, where the *Chemists' Year Book* is referred to as still being published in two volumes, and page 64, Mellor's *Comprehensive Treatise on Inorganic Chemistry* is given as 1922-1925, and Newton Friend's *Text Book of Inorganic Chemistry* as 1917-1920. These, however, are only minor points.

The book, as a whole, is clear and informative, and the style concise and interesting. It should be read and re-read by all young chemists entering or engaged in industry, while many of more mature years would find the time so occupied, well spent.

T. McLACHLAN.

DIE MASSANALYSE. ERSTER TEIL: DIE THEORETISCHEN GRUNDLAGEN DER MASSANALYSE. (THE THEORETICAL FOUNDATIONS OF VOLUMETRIC ANALYSIS.) By Dr. J. M. KOLTHOFF. Berlin: Julius Springer. Price Marks 10.50.

Although there are a number of excellent books, both in the German and English languages, dealing with the practical aspects of volumetric analysis there does not appear to have been, hitherto, any book which dealt adequately with the underlying theory. In the first volume of this new work on volumetric analysis Kolthoff has attempted to gather together in one book all the theoretical matter which has any bearing on the subject. The titles of the chapters are as follows:—Titration curves; Analyses involving neutralisation, precipitation and complex ion formation; Oxidation and reduction reactions and their titration curves; Indicators; Errors of titration; Reaction velocity, catalysis and induced reactions; Adsorption phenomena in precipitation reactions; Volumetric methods in organic chemistry; The permanence of solutions; Review of volumetric methods; and The determination of the "equivalent point." There is also an appendix containing tables of useful data, including solubility products, dissociation constants and electrode potentials.

In the chapter on indicators short accounts are given of the very interesting recent work by Clark on oxidation-reduction indicators and by Fajans on "adsorption indicators." The section on titration errors should prove useful and interesting to analysts; in the opinion of the reviewer this chapter might be extended with advantage. There appears to be no mention of the influence of indicator concentration in neutralisation titration, and many other subjects are only touched on very lightly; but this is just as well, as they are dealt with quite satisfactorily in the author's other books *Indicators* and *Potentiometric Titrations*. (ANALYST, 1927, 254.)

Dr. Kolthoff must undoubtedly be congratulated on collecting together in one volume material on such a diversity of subjects, all of which bear in some way on the theory of volumetric analysis. The book should be of great value to analytical chemists, who are generally apt to be terrified by such expressions as "indicator exponents" and "complexity constants," and should prove very stimulating reading; as the author says in his introduction, a complete understanding of the theory of analysis should lead not only to the improvement of existing methods but to the discovery of new analytical methods. This book is, however, by no means "light" reading; it contains a great deal of material which requires, and merits, careful consideration. Although the book contains a number of references to the scientific literature, it suffers, like most foreign books, from the absence of an index. There are a few misprints, but these are quite obvious.

S. GLASSTONE.

INTRODUCTION TO PHYSIOLOGICAL CHEMISTRY. By MEYER BODANSKY, Ph.D., Associate Professor of Physiological Chemistry, University of Texas. Pp. vi+440. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1927. Price 20s net.

The author, who has set out to write a textbook which will "correlate physiological chemistry with allied sciences" and "to define its scope," may be heartily congratulated on the successful manner in which he has achieved his objects. Dr. Bodansky's introduction to physiological chemistry is, no doubt, one of the most interesting books of its kind, and will find its way into the library of every medical school. All facts are masterfully marshalled, and the arguments clearly reasoned. Moreover, the book is well printed, and, as far as it has been possible for the reviewer to ascertain, free from errors, whether due to the author or the printers.

The book is divided into sixteen chapters, of which Chapter II on the carbohydrates is particularly well written. It gives a concise summary of one of the most complicated chapters in chemistry. Special reference must also be made to Chapter VIII, on physiological oxidations, and Chapter XIII on excretions, both of which make exceptionally good reading. Dr. Bodansky has been most successful in these three chapters. Some of the other sections, especially Chapters X and XI on the intermediary metabolism of fat and protein, are not of the same excellence; they do not show the wide outlook so essential to a text-book of this kind. However, who can cover the whole field of physiological chemistry and do full justice to all its branches?

M. NIERENSTEIN.

THE DYEING OF TEXTILE FIBRES. By R. S. HORSFALL and L. G. LAWRIE. Pp. x+415. London: Ernest Benn, Ltd. 1927. Price 28s. net.

This very useful book on the dyeing of textile fibres marks a new departure in the field of text-books. The authors, without attempting to give all the commercial names of dyestuffs used, try to give a summary of the best methods of

how to dye textile fibres with quite modern dyestuffs. In the introduction there is a summary of our knowledge of colour, together with a description of the most modern methods for the exact measurement of colour. The inclusion of Ostwald's method among those described is very practical, since his method is certainly the best known.

The description of the dyeing of the different textile fibres leaves practically nothing to be desired, and there is also given for each fibre the different types of modern methods of obtaining the fastest dyeings. The authors' full criticisms of the different merits of the dyes are particularly valuable, and are especially interesting in the case of fast cotton dyes. It is astonishing how few of the very many compounds will stand the severest test. Other subjects touched upon include the new methods of immunising cotton, the philana process of Schwarz, and many other important processes in use.

The bibliography is very complete, as is also the index. The authors are to be congratulated upon having chosen new and bright ways of presenting their subject, but the reviewer would have preferred to have had some illustrations, because, as a rule, the student does not know what a jigger or Mather-Platt machine looks like.

H. E. FIERZ-DAVID.

SOME FAMOUS MEDICAL TRIALS. By LEONARD A. PARRY, M.D., F.R.C.S. Pp. x+326. London: J. & A. Churchill. 1927. Price 10s. 6d.

Although the title of this book may suggest that it is exclusively medical in its scope, it is not so in fact, for it consists of a series of very readable accounts of notorious trials in which medical men were being tried, or in which medical matters were at issue. Until comparatively recent times such chemical knowledge as was available was, to a large extent, regarded as coming within the domain of medicine, and was applied to forensic purposes by doctors. Hence it is possible to follow in these pages the gradual evolution of toxicology as a specialised branch of chemistry.

It is interesting to note that many of the toxicological puzzles were first set by criminal doctors. For instance, in the Palmer Case, in 1856, the victim was poisoned by strychnine, which (as Palmer had anticipated), Taylor, the Official Analyst to the Home Office, failed to detect in the body; in the Lamson Case (1881) aconite was given, possibly, as Mr. Justice Hawkins suggested, concealed in the raisin of a cake, and here, again, the medical poisoner banked on the absence of any known chemical tests for aconitine. In like manner in the more recent Crippen case (1911) an unusual poison, hyoscine, was chosen, in the confident expectation that it would not be possible to detect it in the remains. In each of these cases the poisoner was convicted, but a study of some of the trials recorded in this book makes one wonder how many medical poisoners have escaped detection.

Each of the thirty-two chapters is devoted mainly to a particular trial, the circumstances of which are first outlined, after which comes a critical survey of the scientific evidence (some of which is occasionally given *verbatim*) and a short summary of the judge's summing up, the whole being interspersed with the author's comments.

Unfortunately the different trials are mixed up chronologically, so that in successive chapters one jumps from the seventeenth century to the nineteenth, and then back again to the eighteenth, and so on throughout the book; nor is there any sequence in the subject-matter of the trials, poisoning cases being scattered haphazard among forgery cases, libel actions and trials for treason. It is, therefore, not easy to put one's hand rapidly upon any particular incident, especially as the volume lacks an index.

But these are minor details of arrangement, which, though they affect the utility of the book for study or reference, do not detract from its value as a record of scientific cases during the last three centuries or from its readable character. The author has the gift of making his subject live, and he has given us a book which contains a large amount of historical and scientific material presented in an entertaining manner.

EDITOR.

Publications Received.

- MODERN CEREAL CHEMISTRY. By D. W. KENT-JONES. Revised Edition. Liverpool: Northern Publishing Co. Price 25s.
- THE HIGHER COAL-TAR HYDROCARBONS. By A. E. EVEREST. London: Longmans, Green & Co. Price 18s. net.
- THEORETICAL AND EXPERIMENTAL PHYSICAL CHEMISTRY. By J. C. CROCKER and F. MATTHEWS. London: J. & A. Churchill. Price 21s.
- DICTIONARY OF BACTERIOLOGICAL EQUIVALENTS. By W. PARTRIDGE. London: Baillière, Tindall & Cox. Price 10s. 6d. net.
- DIE IODZAHLSCHNELLMETHODE UND DIE UEBERIODZAHLE DER FETTE. By B. M. MARGOSCHES. Stuttgart: F. Enke. Price M 16.20.
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