

THE ANALYST.

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

An Ordinary Meeting of the Society was held on Wednesday, March 2, 1921, in the Chemical Society's Rooms, Burlington House. The President, Mr. Alfred Smetham, was in the Chair.

Certificates were read for the first time in favour of Messrs. Percy N. Mould and W. J. Wright. Certificates were read for the second time in favour of Messrs. Jules Cofman-Nicoresi, Walter K. Fletcher, William Singleton, Francis G. H. Tate, James Darnell Granger, Ph.D., F.I.C., Ed. B. Maxted, Ph.D. (Berlin), B.Sc., and Russell G. Pelly, F.I.C.

Mr. W. R. Schoeller, Ph.D., was elected a Member of the Society.

The following papers were read: "The Acidity of Ink and the Action of Bottle Glass on Ink," by C. Ainsworth Mitchell, M.A., F.I.C.; "The Detection of Adulteration in Butter by Means of the Melting Point of the Insoluble Volatile Acids," by George Van B. Gilmour, B.Sc., A.R.C.Sc.I., A.I.C.; and "Method and Apparatus for Routine Determination of Melting-Points of Fats and Fatty Acids," by S. H. Blichfeldt and T. Thornley.



OBITUARY NOTICES.

ÉMILE BOURQUELOT.

THE death of Émile Bourquelot, on January 31, deprives biological chemistry of one of its most active and distinguished workers. The long succession of papers upon the nature and behaviour of enzymes, which he published during a period of over forty years, and his crowning discovery of the reversibility of enzymic reactions have made his name familiar to chemists all over the world. His investigations on enzymes covered a very wide field, but were mainly concerned with the biology of plants. Many of his communications to French scientific societies had a direct bearing upon analytical chemistry, and were, therefore, abstracted in the ANALYST.

Bourquelot also took an active interest in pharmacy, and since 1900 had been General Secretary of the Société de Pharmacie de Paris, having served as its President in 1898.

EDITOR.

WILLIAM ODLING.

William Odling, who died on February 17, at Oxford, at the age of 92, was one of our earliest Honorary Members, and his death is, therefore, a loss not only to the scientific world, but also in a more intimate degree to our Society.

Odling was born in London in 1829, and began his professional career by taking a medical degree at the University of London, but he soon abandoned medicine for chemistry, and after being chemical lecturer at St. Bartholomew's Hospital, was appointed Professor at the Royal Institution in succession to Faraday. In 1872 he succeeded Sir B. Brodie as Waynflete Professor of Chemistry at Oxford, a position which he held for forty years. He was Secretary of the Chemical Society from 1856 to 1869, and was elected President in 1873, and he was one of the six Past-Presidents whose jubilee was celebrated in 1898.

Among Odling's contributions to theoretical chemistry were various communications developing Gerhardt's doctrine of chemical types, which led to the systematisation of organic chemistry, whilst his practical work included investigations of the compounds of platinum with ammonia and of the compounds of indium. He was also an authority upon the analysis of drinking water, and was one of the official analysts appointed to investigate the London water supply.

At the time of Odling's appointment to Oxford and for many years subsequently, the prevailing conception of the function of University professorships was that they were intended to provide the means and opportunity for research rather than to have an educational aim. The present writer well remembers the controversies that were continually arising over these conflicting views, and how slow was the evolution of the modern idea. Odling, accepting the older view, came but seldom into contact with the younger generation of Oxford chemists, and this was the more regrettable since, apart from the question of personal stimulus, he had as a lecturer the gift of making his subject interesting.

EDITOR.

JOHN CANNELL CAIN.

Dr. John Cannell Cain, whose death occurred suddenly at his residence in Brondesbury Park on Monday morning, January 31, had for the past fifteen years held the office of Editor of the Chemical Society's publications.

He was born at Edenfield, near Manchester, on September 28, 1871, and was the son of the Rev. Thomas Cain, of Stubbins, Lancashire. After receiving his early education at the Manchester Grammar School, he proceeded to the Owens College, where he took the degree of B.Sc. in the Honours School of Chemistry in 1892; thereafter he worked for a year at Tübingen, obtaining the degree of D.Sc. of that University in 1893. Early in his career Cain was drawn towards that field of organic chemistry to which he devoted his life, for in 1895 he began his practical acquaintance with the synthetic dyestuffs by joining Messrs. Levinsteins, Ltd., as a research chemist. In 1901, however, he again reverted to the teaching profession, and became Head of the Department of Physics and Chemistry in the Municipal Technical School at Bury in Lancashire, where he remained until 1904. It was

during this period that he started several important researches on subjects related to the organic dyestuffs, some of which he completed at Bury, leaving others to be finished at a later date elsewhere. It was from here, for example, that he published, with Frank Nicoll, the first three parts of the series on the rate of decomposition of diazo compounds, and as an outcome of this work he obtained the degree of D.Sc. in the University of Manchester in 1904. His appointment as Editor to the Chemical Society was made in 1906, after he had spent the two previous years as manager and head chemist to Messrs. Brook, Simpson, and Spiller, of London.

During his editorship Cain found time to complete many of the researches he had started at Bury, and also to publish several important textbooks. His earliest publication, that of the "Synthetic Dyestuffs," appeared in 1905 in collaboration with the writer, and this was followed in 1908 by the "Chemistry of the Diazo-Compounds," and in 1918 by a book on the "Manufacture of Intermediate Products." He also undertook to revise "Roscoe and Schorlemmer," and published Vol. I. shortly before his death.

During the war Cain placed his services at the disposal of the country, and at the end of 1914 was appointed by Lord Moulton as his first inspector of explosives. He also occupied the position of head chemist to the Dalton Works of British Dyes, Ltd., and was for a time Superintendent of H.M. Factory at Hackney Wick. There is no doubt that his strenuous work during this period was mainly responsible for his early death, because he had a serious breakdown in 1915 which left permanent weakness.

J. F. THORPE.



COMPOSITION OF THE HARROGATE MINERAL WATERS.

By WILLIAM LOWSON, B.Sc., F.I.C.

SINCE the discovery of the Tewit Well by Captain Slingsby in 1571, followed shortly afterwards by that of the Old Sulphur Well and the John's Well, the mineral waters of Harrogate have attracted considerable attention, and now some eighty springs are known, differing in type and quality. These may be divided into two main groups—viz., sulphur waters and iron waters—and each of these two groups is capable of further subdivision.

C. Fox-Strangways ("Memoirs of the Geological Survey," explanation of Sheet 62) gives an extensive bibliography of the literature up to the year 1908, and also an account of the geology of the district. In this he explains the existence of so many springs (no two of which are alike) issuing side by side, as due to the fact that Harrogate is situated at the eastern extremity of the great anticline which traverses this part of Yorkshire; the strata which are bent up by this anticline are the lower members of the Carboniferous series—the Millstone Grit, the shales and sandstones associated with the Harrogate Roadstone and the Mountain or Scar Limestone. The Millstone Grit of this district is for the most part a series of some

half-dozen beds of coarse grits, separated from one another by thick beds of shale. The series of rocks which include the Harrogate Roadstone consist in the upper part of dark blue shales, these being succeeded by thin bands of earthy limestone and chert. These cherty beds rest on dark blue shales containing sulphur, iron, and other chemical substances, and below these again there is a thin rubbly sandstone, also containing sulphur and iron, resting on other beds of shale.

The principal sulphur wells occur about a mile on either side of Harlow Hill, the highest point of the district.

Opinions differ as to whether the waters have a common origin, or whether each spring has its own independent source. The difference of level of adjacent wells favours the view of the separation of the several springs, and the temperatures indicate that they are neither superficial nor come from enormous depths. "Taking all things into consideration it seems the simplest and most probable theory that each spring has its own independent source, with which it is connected by a separate and distinct channel formed by the alternating series of pervious and impervious strata which connects Harrogate with the hilly regions to the west, for it is only from such a source as this that a large body of water could flow year after year, with such slight alteration both in quality and quantity; also that the chemical impregnation of the water is caused during its passage through these strata, and that it is from this source that the bases of all the salts are derived."

A general survey of these waters was undertaken some little time ago by Professor Arthur Smithells of this University, and in connection with this work the author carried out a series of analyses of the more important of them. From time to time in the past there have appeared in different journals accounts of investigations and analyses relating to these springs, and since the data thus recorded have found their way into books and publications of various kinds in many countries, it appears to be desirable to place on record the results of these more recent analyses. The work was commenced towards the end of the year 1912, and the figures given refer to samples collected during that and the two or three succeeding years, the delay in publication being occasioned by the war.

The results are recorded in terms of ionic concentrations.

Further information relating to the different waters is to be found in earlier publications; the following short notes, however, may be of interest: *Old Sulphur*.—A spring situated in the basement of the Old Pump Room; the water percolates through fissures in the Yoredale Rock Stratum, and flows into an artificial basin about 2½ feet deep, and of a similar diameter. *Mild Sulphur*.—Occurs in close proximity to the Old Sulphur Spring, is much less concentrated, and varies considerably in strength from time to time. *Strong Montpellier*.—The well is about 15 feet in depth, and there is usually about 4 feet of water, which is removed by pumping. This water, as well as the Mild Montpellier, shows great variations in strength at different times. *Mild Montpellier*.—The well is about 20 feet in depth, and water accumulates to a depth of about 5 feet. *Magnesia*.—A surface spring occurring at the upper end of the Bogs Field, and fairly constant in composition. *Number 36*.—A surface spring at the lower end of the Bogs Field. *Harlow*.—This is the well commonly known as the Harlow Magnesia Well, and has a depth of 4½ feet.

SUMMARY OF ANALYSES.

Parts per 100,000.

	Old Sulphur Well, Nov., 1912.	Mild Sulphur Well, Nov., 1912.	Strong Montpellier, Dec., 1913.	Mild Montpellier, Apr., 1913.	Magnesia Well, Oct., 1913.	No. 36, Jan., 1913.	Harlow, July, 1915.	Beckwith, Aug., 1915.	Starbeck, Feb., 1914.
Sp. gr. ($\frac{15^{\circ} \text{C.}}{15^{\circ} \text{C.}}$) ...	1.0113	1.0056	1.0076	1.0068	1.0021	1.0033	1.0006	1.0004	1.0019
Total solids ...	1508.5	680.1	1003.3	874.0	258.15	415.7	52.2	45.03	222.3
Sodium ...	506.3	220.25	327.5	300.4	85.7	143.9	10.1	11.04	76.9
Potassium ...	6.5	3.35	4.56	4.51	1.68	2.43	0.66	0.56	0.94
Lithium ...	0.13	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Ammonium ...	1.58	1.16	1.27	0.51	0.29	0.78	—	—	0.27
Magnesium ...	18.24	11.26	15.44	15.49	3.10	4.5	3.62	1.60	2.70
Calcium ...	44.0	23.3	36.86	34.7	78.2	11.09	6.09	3.99	7.35
Strontium ...	Trace	Trace	Trace	Trace	Trace	Trace	—	—	—
Barium ...	6.04	—	0.47	4.9	3.36	1.88	—	—	0.89
Iron ...	—	—	—	—	—	—	—	—	—
Aluminium ...	—	—	—	—	—	—	—	Trace	—
Manganese ...	Trace	—	Trace	—	Trace	—	—	Trace	—
Chloride ...	879.1	382.5	578.0	499.9	134.5	221.2	4.30	3.00	103.5
Bromide ...	2.67	0.9	2.0	1.6	0.4	0.8	—	—	Trace
Iodide ...	Trace	—	—	Trace	—	—	—	—	—
Silicate (SiO ₃) ...	1.20	0.76	1.04	1.11	1.62	1.08	1.21	1.20	1.77
Sulphate (SO ₄) ...	—	11.14	5.73	0.48	0.53	1.65	4.0	—	7.2
Phosphate (PO ₄) ...	—	—	—	—	—	—	—	Trace	—
Carbonate (CO ₃) ...	59.7	53.0	54.9	80.8	67.1	61.4	61.6	46.6	66.15
Sulphur (as Sulphide) ...	8.94	4.85	4.97	6.64	0.68	4.06	0.93	1.18	0.86

Parts per 100,000.

	Kissingen, June, 1914.	Chloride of Iron, Oct., 1914.	Alexandra Chalybeate, Dec., 1914.	Pure Chalybeate, Nov., 1914.	Tewit Well, Mar., 1915.	John's Well, Feb., 1915.	Alum Well, Apr., 1915.
Sp. gr. ($\frac{15^{\circ} \text{C.}}{15^{\circ} \text{C.}}$) ...	1.0071	1.0051	1.0027	1.0001	1.0004	1.0002	1.0028
Total solids ...	988.1	636.3	319.7	12.96	42.15	18.19	358.5
Sodium ...	293.1	207.8	110.4	0.86	1.91	1.46	118.1
Potassium ...	4.33	2.44	2.20	0.27	0.25	0.22	2.05
Lithium ...	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Ammonium ...	—	—	—	—	—	—	—
Magnesium ...	16.80	12.11	3.78	0.66	2.87	1.06	3.97
Calcium ...	41.2	29.44	10.41	1.54	5.60	2.49	10.83
Strontium ...	Trace	Trace	Trace	—	—	—	—
Barium ...	4.80	3.13	2.80	0.06	—	0.06	0.75
Iron ...	1.55	5.05	3.58	0.83	1.71	0.91	3.45
Aluminium ...	—	—	—	—	Trace	—	Trace
Manganese ...	Trace	0.07	Trace	Trace	Trace	0.02	Trace
Chloride ...	578.3	397.3	178.2	1.39	2.29	1.50	186.8
Bromide ...	1.0	1.0	1.0	—	Trace	—	—
Iodide ...	—	Trace	—	—	—	—	—
Silicate (SiO ₃) ...	1.76	1.69	0.97	1.43	2.36	3.13	1.24
Sulphate (SO ₄) ...	1.47	0.13	0.96	0.85	13.96	0.62	6.14
Phosphate (PO ₄) ...	Trace	Trace	Trace	Trace	0.11	Trace	Trace
Carbonate (CO ₃) ...	76.5	41.1	82.0	42.1	35.8	42.03	58.04

Beckwith.—A spring emerging at ground level. *Starbeck.*—The well is about 14 feet deep, and usually contains 2 or 3 feet of water, being fed by springs which emerge from the shales of the Millstone Grit. *Kissingen.*—The well is about 16 feet deep, and is fed by four bore holes sunk in the inclined stratum of shale, and each yielding a water of different composition, hence the water from this well shows considerable variations in strength from time to time. *Chloride of Iron.*—The well is about 15 feet in depth, and is fed by a bore hole 6 feet deep, penetrating the shale which at this point is almost vertical. *Alexandra Chalybeate and Pure Chalybeate.*—These are two surface springs, constantly flowing, and the latter yields the larger volume of water. *Tewit.*—The well is 7 feet in depth, and usually contains about 3 feet of water. *John's.*—A shallow well about 4 feet in depth. *Alum.*—A collection of very superficial water, which is found in the Bogs Field, surrounded by the Sulphur Wells. The yield is small, and for a period of eighty years the site was forgotten, being re-discovered in 1870.

In the case of the Old Sulphur Well it is interesting to note how closely the author's figures agree with those obtained by Thorpe in 1875, and a table of various analyses made during a range of some ninety years by different investigators is appended for comparison, the results here being expressed in terms of grains per gallon :

OLD SULPHUR WELL.

Grains per Gallon.

	West, 1823.	Hunter, 1830.	Hofmann, 1853.	Muspratt, 1867.	Davis, 1872.	Thorpe, 1875.	Lowson, 1912.
Total solids	1024·8	1016·0	1095·919	1108·78	1046·56	1047·013	1055·95
Soda	484·0	471·0	474·054	470·635	—	477·022	477·82
Potash	—	—	33·869	44·165	—	6·063	5·48
Lithia	—	—	—	Trace	—	0·266	0·19
Ammonia	—	—	—	—	—	0·328	1·05
Magnesia	14·7	18·0	23·446	27·392	—	23·839	21·18
Baryta	—	—	—	3·68	—	4·833	4·72
Chlorine	623·9	608·0	650·384	654·908	615·62	613·770	615·37
Bromine	—	—	Trace	Trace	—	1·985	1·87
Iodine	—	—	Trace	Trace	—	0·103	Trace
Silica	—	—	0·251	—	—	0·703	0·66
Sulphur	—	—	6·353	6·737	6·412	6·532	6·26
Sulphuric acid	Absent	Absent	0·101	Absent	—	Absent	Absent
Lime	39·8	43·5	48·243	46·233	—	38·697	43·12
S.G.	1023·24	—	1011·13	—	1011·16	1011·04	1011·28
Carbon dioxide	—	—	—	—	—	35·404	30·66
Free H ₂ S } cubic inches	—	—	5·31	7·01	—	10·16	—
Free CO ₂ } per gallon	—	—	22·03	25·55	—	40·10	—

The author wishes to express thanks to Mr. A. Woodmansey, M.Sc., chemist to the Harrogate Corporation, for information with respect to the depths of the wells.

THE UNIVERSITY, LEEDS.



THE ACIDITY OF INK AND THE INFLUENCE OF BOTTLE GLASS UPON INK.

By C. AINSWORTH MITCHELL, M.A., F.I.C.

(Read at the Meeting, March 2, 1921.)

THE FUNCTION OF ACID IN INK.—The control of the acidity is one of the most important points in the manufacture of iron-gall inks, for it is the principal factor upon which the stability of the preparation depends. In a former communication (*ANALYST*, 1920, 45, 247) I have shown that in the oxidation of ink in the so-called "drying" process there is a gradual change from a soluble ferrous tannate first into colloidal and then into insoluble tannates of iron, and that this oxidation may be accelerated by the presence of certain catalysts. In the case of a mixture of a solution of ferrous sulphate and gall extract, or gallotannic acid, this change takes place fairly rapidly, and deposits and incrustations are formed in the liquid. By adding a certain proportion of strong acid, however, the oxidation process is arrested, and by a suitable regulation of the proportions of the mixture the ink is retained in the form of a stable solution or colloidal suspension until, when applied to the paper, the proportions become so altered by evaporation that the successive changes into the final insoluble resinous iron tannate take place.

AMOUNT OF ADDED ACID IN INK.—It is essential that the quantity of acid added should be kept within definite limits. If too little be added the ink will not acquire the desired stability, whilst if the amount be materially exceeded the ink will have an excessive corrosive action upon steel pens, and the dyestuff used as a provisional colour may even be bleached.

Ink-makers have gradually learned by experience to know the permissible variations of the acidity of their products, but unless this factor be chemically controlled unexpected troubles may occur.

The acids commonly used as stabilising agents are sulphuric, hydrochloric, and oxalic acids, preference being usually given to hydrochloric acid. In the German standard ink 2.5 parts of hydrogen chloride are added to 1,000 parts of ink. This formula has also been adopted for use as a comparative standard in the United States specifications for writing ink (*ANALYST*, 1921, 61). The British Government specifications, which were issued a few months ago, fix standards for the proportion of iron, but no reference is made to the acidity of the inks.

INKS WITHOUT ADDED ACID.—Several manufacturers prepare an ink to which no addition of strong acid is made. These consist essentially of iron gallate or of a complex iron gallate, for solutions of such salts when exposed to the air do not undergo the changes to which solutions of ferrous tannate are liable. A solution of gallic acid and ferrous sulphate is practically stable under conditions that will cause a solution of gallotannic acid and ferrous sulphate to yield deposits and incrustations. For example, I exposed a solution of 3 grms. of gallic acid and 2 grms. of ferrous sulphate to the air for thirty-five days and only obtained a deposit

of 0.036 grm., whilst the filtrate on further exposure for weeks yielded only a slight trace of deposit.

Hence a gallic acid ink has the advantage over an iron-gall ink of not requiring the addition of acid, and so of having little, if any, corrosive action upon a steel pen, although this point is not of importance in the case of fountain-pen inks, which are intended to be used with pen-nibs not attacked by dilute acid. On the other hand, the general opinion of practical inkmakers with whom I have discussed the subject is that gallic acid inks lack "body" and do not penetrate the fibres of the paper so readily as acidified gallotannic inks. The low proportion of solid matter in some of these inks is attributable to the small solubility of gallic acid in water (about 0.5 per cent. at 15° C.), which also limits the proportion of iron which can be introduced into the ink. Some of the oxyferrigallates are more soluble than ferrous gallate, but I am doubtful whether it would be possible to prepare a standard ink containing the 0.5 per cent. of iron required by the British Government specifications solely by the use of gallic acid.

The other question of the alleged inferiority in penetrating power of gallic acid inks could probably be definitely decided by comparative microtome tests.

EFFECT OF FERROUS SULPHATE ON THE ACIDITY.—The final composition of the ink depends to a considerable extent upon the copperas used in the manufacture, and variations in this salt may also have an influence on the acidity.

Theoretically, ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, contains 20.08 per cent. of iron. The presence of iron in excess of this amount is usually due to crystallisation of the salt at higher temperatures. Various commercial samples of copperas which I have examined during the last two or three years have contained the following amounts of iron: (1) 19.43; (2) 18.77; (3) 25.92; (4) 20.43; and (5) 19.36 per cent.

In nearly every instance the manufacturer's price was proportional to the amount of iron in the salt, and practical tests showed that an ink prepared from samples such as No. 2 would contain too little iron, if the calculation had been based on the use of a 20 per cent. copperas.

Commercial copperas has almost invariably a slight acid reaction. The acidity of the above-mentioned samples, in terms of *N*-alkali, varied from 0.11 to 0.37 c.c. per 1 grm. Obviously this acidity increases the amount of strong acid in the final ink, and accounts for the presence of such acid in inks to which no mineral acid has been added as such.

In estimating the acidity of copperas the ordinary indicators, such as litmus or phenolphthalein, are not of much use, since, unless added in very large quantity, they are bleached. Better results are obtained by titrating the solution without any indicator, the end-point being shown by the liquid turning bluish-green as soon as the precipitation of ferrous hydroxide begins. Houben's method (*Ber.*, 1919, 52, [B], 1623) of using ferrous sulphide as an indicator is not satisfactory.

Another way in which the ferrous sulphate may influence the acidity of the ink is through the formation of a basic salt. Copperas which has undergone superficial oxidation, with the formation of a coating of yellow basic sulphates, is technically termed "rusty," and is usually preferred by ink manufacturers, probably owing to the fact that the use of such salt accelerates the darkening process in the ink. Such

copperas may show pronounced acidity, and yet still neutralise added acid, so that an ink made from "rusty" copperas may show a different acidity from one prepared from the fresh green salt.

ESTIMATION OF STRONG ACID IN INK.—The presence of the blue dyestuff used as provisional colouring matter renders direct titration of ink very uncertain. Electro-metric titration would probably give satisfactory results, but the conditions would have to be worked out for each kind of ink. That is to say, the conditions for a hydrochloric acid ink would differ from those required by an oxalic acid ink, and in every case a method would have to be devised to distinguish between the strong acids and the weak organic acids in ink.

The only method hitherto described for estimating strong acids in ink is the somewhat crude one of immersing a weighed pen nib in a measured quantity of the ink, and estimating the amount of metal dissolved. This method, which I devised some years ago and published in my book on inks, has recently been included in the United States specifications (*supra*) without acknowledgment.

A much more accurate and rapid method is to distil 10 c.c. of the ink with an excess of a neutral solution of sodium acetate, and to titrate the acetic acid in the distillate. The objection to the process is that it requires at least three distillations of portions of about 100 c.c. each to expel practically the whole of the acetic acid, for Leeds (ANALYST, 1895, 20, 224) and subsequently Brode and Lange (ANALYST, 1909, 34, 157, 1909, 30) have shown that traces of free acetic acid are obstinately retained by organic matter. Distillation with xylene as a carrier, as suggested by Pickett (*J. Ind. Eng. Chem.*, 1920, 12, 570), does not offer any advantage in this case.

ESTIMATION OF THE TOTAL ACIDITY.—The method that I have found to be the most satisfactory means of estimating both the added acid and the weak organic acids in ink is to bleach the pigments with hydrogen peroxide as follows: Five c.c. of the ink are boiled for a few minutes with 10 c.c. of the ordinary 10 vol. hydrogen peroxide solution beneath a reflux condenser, the flask being continually shaken until a pale straw-coloured solution is obtained. This is cooled, diluted with three or four times its volume of water, and titrated with *N*-alkali solution, with phenolphthalein as indicator. A blank test is also made with 10 c.c. of hydrogen peroxide diluted with 10 c.c. of water, and the acidity deducted from the previous result.

I have proved by experiment that the hydrogen peroxide treatment does not oxidise any constituents of gall extract into acids, which would otherwise increase the acidity of the ink.

APPLICATION OF THE METHOD TO LOGWOOD INKS.—Hæmatoxylin, the colouring matter of logwood, is not bleached when boiled with hydrogen peroxide, and the method is therefore not directly applicable to logwood inks. Hence, in the case of such inks it is necessary to use the following modification of the method: Five c.c. of the ink are boiled with 20 c.c. of hydrogen peroxide solution and 2 c.c. of *N*-sodium hydroxide solution for about five minutes, until the liquid becomes transparent and pale. It is then cooled, diluted with a large volume (five or six times) of water, and the excess of alkali titrated with standard sulphuric acid, with Congo red as indicator (litmus or phenolphthalein being bleached). As before, a blank test

is made to determine the correction to be applied for the acidity of the hydrogen peroxide.

No acids are formed when hæmatoxylin is boiled with the alkaline hydrogen peroxide, and sulphuric acid added to such a solution can be accounted for quantitatively after the treatment. In the case of Antoine's ink (No. 1 in the table), which is a logwood ink, it is interesting to note that the total acidity estimated by the hydrogen peroxide method is very slightly lower than the acidity due to strong acids, as found by the distillation method.

ACIDITY OF COMMERCIAL INKS.—The following results were obtained by means of the methods described with representative samples of commercial inks, the results in each case being expressed in terms of c.c. of *N*-alkali neutralised by 10 c.c. of ink.

Ink.	Total Acidity.	Strong Acids.	Weak Acids.
	c.c.	c.c.	c.c.
1. Antoine, Violet black	1·60	1·76	nil
2. Arnold, Blue-black	1·93	0·30	1·63
3. Blackwood, "Record"	5·62	1·55	4·07
4. Cochran's Blue-black (1912) (heavy deposit) ...	1·93	0·60	1·33
5. " " Acid-free ink	3·10	0·01	3·09
6. Field's Blue-black, old	2·66	—	—
7. " " " " , new	2·99	0·17	2·82
8. Hollidge, Blue-black (heavy deposit)	7·0	0·40	6·60
9. Mordan's "Azuryte"	4·06	0·98	3·08
10. Morrell's Blue-black (faded, heavy deposit) ...	1·92	0·07	1·85
11. Stephen's Blue-black	3·83	2·46	1·37
12. "Swan"	3·42	1·82	1·60
13. Typical Blue-black ink (deposit), April	3·20	—	—
(a) " (faded), August	0·15	—	—
(b) " (alkaline), January	-0·30	nil	—
14. Tarling, Blue-black	3·85	1·35	2·50
15. Webster "Diamine ink" (old, heavy deposit) ...	0·48	0·08	0·40
16. " " " (new)	3·68	0·18	3·50

ACIDITY CONTROL OF THE MANUFACTURING PROCESS.—The hydrogen peroxide method affords a simple method of controlling the correctness of the manufacturing process. For example, in the case of an ordinary iron-gall or gallic acid ink prepared by a specified formula the total acidity remains fairly constant from month to month. Any pronounced variation from this figure will point either to some deviation from the formula, or to the action of some external influence.

Last year complaints were received by different manufacturers of ink of the occurrence of deposits in the bottles, and in some of the worst cases the ink itself had faded. The composition of the ink was in most cases normal, with the exception of the acidity being somewhat lower than usual, and it therefore appeared as though the ink had been sent out insufficiently matured, so that a deposit which should have formed in the vats had formed in the bottles.

It was not until I examined a bottle in which the colour of the ink had changed to a dirty brown that I found that there was something radically wrong. In that case the total acidity by the peroxide method was only 1.5 c.c., or rather less than half the normal value. As there was no evidence of contamination with an alkaline salt, I tested the glass of the bottle itself, and this gave me the solution of the problem. It was not the ink, but the bottle which was at fault.

INFLUENCE OF ALKALINE GLASS.—When cold distilled water was placed in the empty bottles, after thorough cleaning, or when the bottles were immersed in water, alkali was rapidly dissolved, and, after about five minutes, the water showed a pronounced alkaline reaction towards phenolphthalein.

Two series of tests were made with two new bottles of the same consignment. Each was filled with water, and 10 c.c. portions were titrated with *N*-sulphuric acid at subsequent periods, with the following results: I. After 4 hours, 0.47 c.c.; after 24 hours, 0.94 c.c.; after 48 hours, 0.94 c.c.; after 72 hours, 0.94 c.c.; and after 9 days, 0.47 c.c. II. After 3 days, 0.71 c.c.; 13 days, 0.75 c.c.; 20 days, 0.66 c.c.; and 24 days, 0.14 c.c.

It appeared, therefore, that the reaction was retrogressive, the alkali first liberated by the water from the sodium silicate or the alkali carbonate dissolved again entering into combination with other constituents of the glass.

An analogous test was made by placing 18.9 c.c. of *N*-sulphuric acid in bottle No. 1. After eleven days the acidity had fallen to 12.8 c.c.

The same effect is produced by ink, as is seen by the results given by the sample No. 13, in which the change was followed from an acidity of 3.2 c.c. to an alkalinity of 0.30 c.c.

Nor does ink free from added acid fare any better when placed in these bottles. For instance, a sample from a bottle of Field's ink, the bulk of which is still quite free from any deposit, produced a thick incrustation on the sides of one of these bottles within three days, whilst its total acidity, as determined by the hydrogen peroxide method, fell from 2.99 c.c. to 0.35 c.c. in sixty days, and the colour changed from bright blue to brownish purple.

The explanation offered by the makers of these glass bottles was that owing to their being unable to obtain supplies of salt-cake they had used soda-ash in the manufacture of this glass, and had thus introduced an excess of alkali. Incidentally they suggested that probably all bottle glass would be found to be more or less alkaline. Although the term "alkalinity" may be regarded as relative in this connection, some bottle glass, at all events, is practically neutral, for I have kept standard sulphuric acid for several years in a bottle without its showing more than the slightest depreciation.

At the same time, it is quite possible that the cheaper kinds of glass bottles, such as are used for ink, may not infrequently yield a considerable proportion of free alkali to any liquid placed in them, and that this may be the hitherto unsuspected reason for the occasional deterioration of ink in bottle.

This was borne out by an experiment with the bottle which had contained the faded, decomposed Morrell's ink (No. 10). After thorough washing, the bottle was filled with distilled water, and the liquid tested daily. For five days it remained

neutral to phenolphthalein, but on the sixth day gave a very faint pink coloration, and on the seventh day a distinct alkaline reaction. Hence, although this glass was much less alkaline than that of the bottles mentioned, it seems reasonable to conclude that in this instance, also, it was the cause of the instability of the ink.

The glass of the very alkaline bottles was distinctly vitreous in character, but this less alkaline glass was much clearer, and it is possible that a relationship might be established between the alkalinity and the transparency of glass.

If the alkalinity of bottle glass be as common as these glass manufacturers suggest, it may have an important bearing upon other products. For instance, the 33 per cent. acetic acid of the British Pharmacopœia would soon be reduced below the standard strength if sent out in bottles of this type, whilst such glass might cause the precipitation of quinine from pharmacopœial preparations of quinine salts.

In chemical work my chief difficulties have been caused, not by the alkalinity of glass bottles, but by the solution of iron from the glass by acids, this being particularly pronounced in the case of Winchester quart bottles. After some time hydrochloric acid has become quite yellow from this cause, and has given a strong Prussian blue reaction.

In conclusion, I wish to thank Messrs. Mabie, Todd and Co. for permission to bring before you such of these results as were obtained in the routine examination of their inks.

DISCUSSION.

DR. R. D. BAIN asked whether the author did not find that the action of hydrogen peroxide on some inks tended to increase the acid. Hæmatoxylin, for instance, when oxidised under suitable conditions, gave formic acid. Might it not be possible that intermediate acids were formed during the boiling with hydrogen peroxide? The excessive alkali shown in some of the bottles might be due, not so much to the excess of alkali in the glass, as to the degree of resistance of the glass to corrosive action. The proportion of saltcake to soda ash in the constitution of a glass had an influence upon the skin for resisting purposes. But the substitution of saltcake for soda-ash, or *vice versa*, did not have any material influence on the final alkalinity of the glass. It was the proportion of alkali to lime that could change the alkalinity of the glass; and this was largely a question of expediency in the glass bottle trade. The introduction of machine-made bottles into England had necessitated a change in constitution, and "sweeter" glass was required for machine-made bottles than for hand-made bottles.

He wished to draw the author's attention to the work of Wood, Sand, and Law (*J. Soc. Chem. Ind.*, 1911) where these investigators used the electrometric titration method for the investigation of dark tanning liquids. It appeared to him that the determination of acidity by means of the concentration of H-ions would not only render one independent of the colour of the liquid for the final point, but might possibly give a more rapid estimation.

Mr. G. RUDD THOMPSON inquired whether, in view of the importance of an acid-free copperas to ink manufacturers, it would not be possible to use ferrous ammonium

sulphate instead of the ordinary ferrous sulphate. There would be no difficulty in providing supplies of the double salt.

Dr. G. MONIER-WILLIAMS emphasised the advantages of electrometric methods of titration. Since the acidity due to strong acids in the ink appeared to be the important point, he wished to know what advantage was gained by determining the acidity due to the weak organic acids.

Mr. E. T. BREWIS remarked that it was fairly well known that the "metal" of which such cheap bottles as those exhibited were made was partially soluble in distilled water, yielding an alkaline solution. Very cheap bottles were made from "cullet," and sometimes, as in the case of Yorkshire cullet, the pot was "flashed" with soda-ash to lower the fusion point of the metal. The bubbles and flaws in the bottles passed round were due to imperfect fusion, and the alkalinity of the glass might be due to an attempt to rectify those faults by the addition of soda rather than by expenditure of fuel. It might be of interest to mention that the greatest care was necessary in selecting the glass tubing used for making "ampoules" for sterile sera and alkaloidal solutions, the slightest trace of alkalinity causing such solutions to deteriorate on storage.

Mr. T. F. HARVEY pointed out that methyl red could be used as a satisfactory indicator for the alkalimetric titration of ferrous sulphate solutions.

Mr. MITCHELL, replying to Dr. Bain, remarked that the difficulty with regard to electrometric titration was that a separate standardisation would be necessary for each kind of ink. For any given kind of ink, however, it would probably be a very satisfactory method of factory control. Within the limits of his experience he had not found that oxidation of hæmatoxylin occurred in the peroxide method, and a small addition of sulphuric acid to a logwood solution could be estimated quantitatively. The advantage of estimating the total acidity of the ink was that it served as a control of the factory operations, any variation from the formula being immediately indicated. Referring to Mr. Thompson's suggestion of the use of ferrous ammonium sulphate in place of ferrous sulphate, he said that he had already made a series of experiments with the former salt, the results of which had indicated that the double salt would be a satisfactory substitute for ordinary copperas. A slight variation in the acidity of ferrous sulphate was not a matter of great importance for an ordinary acidified iron-gall ink, but in the case of non-corrosive gallic acid inks, it was essential that no strong mineral acid should be present.



ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Iron as the Cause of the Formaldehyde and Diphenylamine Reaction of Milk. F. Reiss. (*Zeitsch. Unters. Nahr. Genussm.*, 1921, **41**, 26-29.)—The presence of iron in milk causes the latter to yield a reaction with diphenylamine sulphuric acid similar to that given by nitrates or nitrites. Milk may become contaminated with iron when it is kept in rusty churns or cans, and if iron be detected by the ferrocyanide reaction the test for nitrates should be applied to the milk serum (obtained by allowing the milk to curdle spontaneously) and not to the milk itself.

W. P. S.

Mustard Oil as a Milk Preservative. P. Post. (*Pharm. Weekblad*, 1921, **58**, 131-138.)—Mustard oil may be added to milk, in the proportion of 20 drops per litre, as a preserving agent. The treatment has no influence on determinations of specific gravity, fat, acidity, total solids, ash, chlorides, nitrates, preservatives, specific gravity and refraction of the serum, or the polarisation. Addition of mustard oil depresses the freezing-point; with a high fat content the error is small, and it may be almost entirely eliminated by one agitation with 10 per cent. of sesamé oil. In lactose estimations the mustard oil must first be removed by shaking the milk three times with petroleum spirit, and for the determination of albumin the sample must be evaporated to half its bulk. Catalase is decomposed by mustard oil.

W. J. W.

Coffee Extracts. G. S. Ponce and J. R. Palma. (*Bol. Lab. Municipal de Guayaquil*, 1920, **1**, 65.)—Twenty-four samples of genuine coffee extract contained from 9.04 to 11.91 per cent. of water (average 10.62); 82.69 to 85.05 per cent. of organic substances (average 83.68); and 4.92 to 6.66 per cent. of ash (average 5.61 per cent.).

Composition of Chicha. C. D. Andrade. (*Bol. Lab. Municipal de Guayaquil*, 1920, **1**, 71-74.)—Chicha is a fermented beverage, prepared from maize, which is largely used by the working classes in Guayaquil. In the course of its manufacture toxic nitrogenous putrefaction products are formed, and to these are attributed the poisonous effects of the drink upon certain individuals. Ten samples had the following composition: Acids (as tartaric acid), 4.15 to 8.70; alcohol, 26.5 to 54.63; sugars (dextrose and invert sugar), 7.65 to 9.17; nitrogenous substances, 5.98 to 6.40; glycerol, 4.05 to 4.70; and mineral matter (ash), 2.59 to 2.87 grms. per litre.

Estimation of Sugar in Wine. W. Fresenius and L. Grünhut. (*Zeitsch. anal. Chem.*, 1920, **59**, 415-457.)—With non-hydrolysed wines of acid reaction, lead acetate may be employed as a clearing agent, if not in excess. In the case of wines

which have been hydrolysed by hydrogen chloride, and are acid, lead acetate may be used for precipitation of the chlorine, but other impurities cannot be removed. After neutralisation these can indeed be precipitated by excess of lead acetate, but a loss of sugar then results in presence of chlorides. It is therefore preferable either to substitute bone black for the lead acetate, or, if the latter be used, to precipitate the chlorine ions first by means of another reagent, such as silver nitrate. W. J. W.

Preparation of Rhamnose. C. F. Walton, jnr. (*J. Amer. Chem. Soc.*, 1921, 43, 127-131.)—Rhamnose may be prepared conveniently in the laboratory from "flavin," a commercial product rich in quercitrin, the flavin being hydrolysed by boiling it for thirty minutes with 10 parts of water and 0.5 per cent. of sulphuric acid (calculated on the flavin plus water), the residue washed free from sugar, and the combined filtrates neutralised with barium carbonate, decolorised, and concentrated under diminished pressure until containing about 40 per cent. of solids. The inorganic impurities are then precipitated by the addition of alcohol, and the filtrate concentrated until it contains 70 to 80 per cent. of solids, and allowed to crystallise; the yield of rhamnose is 20 to 25 per cent. of the flavin taken. T. H. P.

Volumetric Method for the Estimation of Lactose by Alkaline Potassium Permanganate. F. T. Adriano. (*Philippine J. Sci.*, 1920, 17, 213-220.)—The following method is described for the estimation of lactose by oxidation with alkaline potassium permanganate solution. Twenty-five c.c. of the milk are mixed with about 400 c.c. of water, 10 c.c. of Fehling's copper sulphate solution are added, the mixture is nearly neutralised with sodium hydroxide solution, diluted to 500 c.c., and filtered. Ten c.c. of the filtrate are mixed with 50 c.c. of $\frac{N}{10}$ permanganate solution and 25 c.c. of 0.848 per cent. sodium carbonate solution, the mixture is diluted to 100 c.c., and heated, the temperature being raised to 95° C. in two minutes and maintained for a further two minutes. Twenty-five c.c. of 30 per cent. sulphuric acid are added and $\frac{N}{10}$ oxalic acid is introduced until the solution is clear; the excess of oxalic acid is then titrated with the permanganate solution. The amount of permanganate used for the actual oxidation is a measure of the quantity of lactose present, this quantity being found by reference to the table given below :

Lactose.		Lactose.		Lactose.		Lactose.	
$\frac{N}{10}$ KMnO ₄ .		$\frac{N}{10}$ KMnO ₄ .		$\frac{N}{10}$ KMnO ₄ .		$\frac{N}{10}$ KMnO ₄ .	
Mgrms.	C.c.	Mgrms.	C.c.	Mgrms.	C.c.	Mgrms.	C.c.
1	2.51	11	12.30	21	23.63	31	34.65
2	3.21	12	13.80	22	24.87	32	35.69
3	4.04	13	15.41	23	25.92	33	36.16
4	4.39	14	16.72	24	26.67	34	37.26
5	5.47	15	17.85	25	28.10	35	38.26
6	6.52	16	19.04	26	28.39	36	38.64
7	7.69	17	20.16	27	29.50	37	39.28
8	9.13	18	20.96	28	30.60	38	40.16
9	9.98	19	21.50	29	31.49	39	40.56
10	11.37	20	22.89	30	32.55	40	41.47

The results obtained are concordant, but slightly lower than those obtained by the Soxhlet method.

W. P. S.

Composition of Palm Kernels from Madagascar. G. Clot. (*Chem. Abstracts*, 1921, **15**, 184, from *Mat. grasses*, 1920, **12**, 5661-5662.)—*Hyphane shatan* seeds gave the following analytical results: Moisture, 12.10; fat, 8.08; total ash, 2.39; soluble ash, 1.01; cellulose, 71.48; and nitrogenous substances, 5.95 per cent. The oil derived from the seeds gave an iodine value of 21.9, and saponification value 245.3; and hydrolysis of the cellulose yielded 24.7 per cent. of mannose and 9.65 per cent. of dextrose. *Borassus Madagascariensis* seeds gave: Moisture, 10.25; fat, 0.51; total ash, 1.74; soluble ash, 1.20; cellulose, 82.66; and nitrogenous substances, 4.84 per cent. Hydrolysis of the cellulose yielded 36.36 per cent. of mannose and 8.8 per cent. of dextrose.

T. J. W.

Analysis of Otoba Butter. W. F. Baughman, G. S. Jamieson, and D. H. Brauns. (*J. Amer. Chem. Soc.*, 1921, **43**, 199-204.)—The sample of otoba butter (from *Myristica otoba*) examined was brown and of disagreeable odour. It contained 9.3 per cent. of essential oil, 20.4 of other unsaponifiable matter, and 67.6 of fatty acids, and its constants were: Sp. gr., 0.9293 at 20°/20° C.; refractive index, 1.4710 at 40° C.; iodine number (Hanus), 54.0; saponification value, 185.0; and m.-pt., 34.0° C. The essential oil, separated by steam distillation, had a slight odour and a yellow colour, the latter fading in the light; it consisted chiefly of sesquiterpenes, and had density at 20° C. 0.89067, $[\alpha]_D^{20} - 32^\circ$ and $n_D^{20} 1.4180$. The glycerides present in the butter were those of lauric (15.1 per cent.), myristic (52.2), palmitic (0.2), and oleic acids (3.9); and the unsaponifiable constituents, besides the essential oil, consisted of a viscous yellow mass (11.0 per cent.) and of the isomeric otobite and iso-otobite, $C_{20}H_{20}O_4$ (9.4 per cent. together). Otobite (m.-pt., 137-138° C.) and iso-otobite (m.-pt., 106-108° C.) both give with concentrated sulphuric acid a pink coloration, which becomes very intense on standing and persists for days. Addition of several drops of concentrated sulphuric acid to glacial acetic acid solution of either compound (phytosterol test) gradually produces a pink coloration, which turns somewhat purple after some hours and persists for some days. Attempts to obtain acetyl derivatives or to methylate the compounds with methyl sulphate were unsuccessful, whilst treatment with alcoholic potassium hydroxide solution and fusion with potassium hydroxide were without effect. Otobite contains one methoxyl group in the molecule, but iso-otobite none. Both compounds form pentabromides, $C_{20}H_{20}O_4Br_5$, (m.-pt., 190° C. and 191° C. respectively).

T. H. P.

Grape Seed Oil. E. Klinger. (*Chem. Abstracts*, 1921, **15**, 181; from *Farben-Zeit.*, 1920, **26**, 6.)—Examination of a pure sample of grape-seed oil gave the following results: Sp. gr. 0.925; saponification value, 192; iodine value, 130.9; whilst the fatty acids gave neutralisation value, 199.5; iodine value, 133.5; m.-pt., 23°-25° C.; and solidifying point, 18°-20° C. The oil dried to a sticky film in four days, and in a shorter time when mixed with metallic driers. The oxygen absorption was 7 per cent. in four days, whilst a control, using linseed oil, showed 14.7 per cent. On being

heated to 300° C. the oil developed "body" more rapidly than linseed oil, and in a few hours became a gummy mass.

T. J. W.

New Hydroxystearic Acid from Hardened Castor Oil. H. Thoms and W. Deckert. (*Ber. Deut. Pharm. Ges.*, 1921, 31, 20-26.)—From a sample of hardened castor oil (m.-pt., 80° C.; iodine value, 12) boiling alcohol extracts 1-12 hydroxystearic acid, $\text{CH}_3[\text{CH}_2]_5\text{CH}(\text{OH})[\text{CH}_2]_{10}\text{CO}_2\text{H}$ (m.-pt., 83° C.; iodine value, 0). The ethyl ester of the acid was prepared, as well as the anilide and *o*-toluidide, the corresponding ketostearic acid formed on oxidation, and other derivatives.

T. H. P.

Bombay Mace. (*U.S. Dept. Agric. Bureau of Chemistry, Service and Regulatory Announcements*, No. 26, 21-22.)—Although "Bombay mace" closely resembles true mace in appearance, and is botanically a mace, it is practically devoid of flavour, and is useless as a spice. Its use in spices is merely as a filler and adulterant, and the Bureau of Chemistry is of the opinion that it should not be used as an ingredient of spices, even when these are labelled to show its presence.

R. G. P.

Changes produced in Wheat by Tempering. E. L. Tague. (*J. Agric. Research*, 1920, 20, 271-275.)—"Tempering," also known as "dampening" or "conditioning," consists in mixing water with the wheat and allowing the mixture to stand for some time before grinding. This treatment toughens the bran coat, produces an increased yield of flour, and enables better bread to be made. Several kinds of tempered wheat were ground, and a quantity of the flour equivalent to 50 grms. of dry material was added to ten times its weight of water at 40° C., 2 c.c. of toluene being added as preservative. The mixture was well shaken and maintained at 40° C. for two hours, with occasional shaking, after which it was whirled in a centrifuge for five minutes, the liquid filtered, and the filtrate examined. Tempering at 20° C. produced a slightly higher P_H value and a slight increase in the total acidity, water-soluble phosphorus, and "titratable nitrogen" (c.c. of $\frac{N}{10}$ NaOH required to titrate 10 grms. of flour), and the increase was still more pronounced at 40° C. The chemical changes increased with an increase in the time of tempering, but were detrimental after a period of forty-eight hours.

T. J. W.

Bleached Flour in U.S.A. (*U.S. Dept. Agric. Bureau of Chemistry, Service and Regulatory Announcements*, No. 26, 21.)—The Bureau regards as adulterated flour bleached by any process, if the bleaching has reduced the quality or strength or has concealed damage or inferiority. Bleached flour may, however, be shipped within the jurisdiction of the U.S.A. Food and Drugs Act if it satisfies the above requirements, provided that it is branded to indicate that it has been bleached. No action will be taken at the present time on the ground that bleaching introduces into the flour a substance which may be injurious to health, provided, as a result of bleaching, there is not introduced such a quantity of the bleaching agent as may render the flour injurious as indicated in a decision of the Supreme Court.

R. G. P.

Action of Halogen Acids on Oil of Juniper. R. Huerre. (*J. Pharm. Chim.*, 1921, **23**, 81-89.)—The crystalline compounds, obtained by treatment of oil of juniper with halogen acids, consist entirely of hydrochloride, hydrobromide, and hydriodide of cadinene. Treatment with acetic acid saturated with hydrogen iodide yielded, with three samples, 54 and 69 per cent.; 37.75 and 36.20 per cent.; and 37.50 and 51.25 per cent. of crystals. The relative amounts obtained with hydrogen iodide, bromide, and chloride were, in the case of one sample, 54 and 69, 24, and 12.40 per cent.; and with another sample, 44, 28, and 18.15 per cent. The respective yields obtained from equal quantities of cadinene were 18.15 per cent. of hydrochloride, 23.98 per cent. of hydrobromide, and 30.14 per cent. of hydriodide. An approximate estimate of the amount of cadinene (laevorotatory) in oil of juniper may be obtained from the yield of hydriodide: $C_{15}H_{24} \cdot 2HI$. This may attain a maximum of 30.59 per cent., but the average figure is 21.11 per cent. W. J. W.

Estimation of Thymol: Spanish Oil of Thyme. H. Mastbaum. (*Chem. Zeit.*, 1921, **45**, 18-19.)—Three successive extractions with 100, 80, and 50 c.c. of 5 per cent. sodium hydroxide solution, remove the phenols (thymol and carvacrol) from 25 grms. of the sample. The extracts are made up to 250 c.c. and filtered; 200 c.c. are rendered acid and cooled, and the oily layer is separated and weighed in a tared beaker; on stirring, the crystallisation of the thymol usually begins without inoculation. The crystals are collected on a weighed filter, pressed between paper, and weighed. Eight samples of Spanish oil of thyme had: Sp. gr. 0.9444 to 0.9747 at 15°/15° C., and contained 55 to 67.5 per cent. of phenols. O. E. M.

Estimation of Thymol in the Volatile Oil of *Mosla japonica*. T. Kariyone and K. Atsumi. (*J. Pharm. Chim.*, 1921, **23**, 148-149.)—The volatile oil of *Mosla japonica* contains *p*-cymene, thymol, and another phenol, probably carvacrol, and is the most important Japanese source of thymol. For the estimation of thymol, 10 c.c. of oil are dissolved in 40 c.c. of petroleum spirit, and extracted by shaking four times successively with 10 c.c. of sodium hydroxide solution 5 per cent.; the phenols are liberated from the alkaline liquid by acidification with 30 c.c. of hydrochloric acid (15 per cent.) and crystallised by cooling and, if necessary, by adding a crystal of thymol. The crystals are drained and, after washing with 20 c.c. of dilute alcohol (10 per cent.) and then with 30 c.c. of cold water, are dissolved in sodium hydroxide solution (5 per cent.), and made up to 500 c.c. The thymol in 10 c.c. of this liquid is estimated iodimetrically. If more than 32 per cent. of liquid phenols be present in the mixed phenols the method is useless, but where less than 9 per cent. is present (as in the oil in question) the error of determination does not exceed 2 per cent. R. G. P.

Extraction of Thymol and Carvacrol from Alkaline Solutions. D. C. L. Sherk. (*Amer. J. Pharm.*, 1921, **93**, 8-18.)—Both phenols are extracted in the free state from alkaline solution by shaking with ether, heptane, benzene, carbon tetrachloride, or carbon disulphide. The extraction of 50 c.c. of 5 per cent. sodium hydroxide solution containing 7.46 grms. of thymol with three successive 50 c.c.

portions of solvent gave the following percentages of the original thymol extracted: Ether 99.7, heptane 29.9, benzene 67.9, carbon tetrachloride 52.6, and carbon disulphide 66.2. Thymol recovered by the use of carbon disulphide was of more satisfactory appearance than when other solvents were employed. Increasing the concentration of sodium hydroxide in the aqueous solution has no effect upon the ether extraction, and but little effect when benzene or carbon disulphide is used, but the results with heptane and carbon tetrachloride are considerably affected. Thymol showed considerable deliquescence to ether vapour, but not to the vapours of the other solvents employed.

T. J. W.

Constituents of "Shê-chuang-tzu" (*Selinum Monnieri* L.) M. Nakao. (*J. Pharm. Chim.*, 1921, **23**, 141-142.)—This drug, known in Japan as "dsha-sho-shi" and composed of the fruits of *Selinum Monnieri* L., is held in repute in China as an aphrodisiac and as a sedative. On steam distillation it yielded 1.3 per cent. of a yellowish limpid volatile oil with a turpentine-like odour; sp. gr. at 15°/15° C., 0.896; $[\alpha]_D^{20} - 42.7^\circ$; acid value, 1.63; saponification value, 23.62; and saponification value after acetylation, 51.35. Potassium hydroxide and bisulphite solutions did not dissolve any of the oil. The following fractions were separated: (1) 154-157° C., $[\alpha]_D^{20} - 55.42^\circ$ contained *l*-pinene; (2) 157-160° C. contained camphene; (3) 200-250° C., $[\alpha]_D^{20} - 33.14^\circ$; this consisted principally of an ester having a saponification value of 229 and yielding *l*-borneol and iso-valeric acid. The fractions of high b.-pt. gave a small quantity of crystals not identified. Phellandrene, cineol, and terpineol were not present.

R. G. P.

***Polygonum Bistorta* as a Substitute for *Krameria triandra*. Ruiz and Pavon.** (*Chem. Abstracts*, 1921, **15**, 144, from *J. Pharm. Belg.*, 1920, **2**, 876-878.)—Analysis of *Polygonum* gave the following results: Water, 6.3; ash, 4.35; tannic acid, 18.25; reducing sugars, 2.13; gums, 2.23; and starch, cellulose, and resin, 66.74 per cent. When tested with ammonium molybdate all the tissues were found to contain tannin, but the amount was greatest in the cortical parenchyma. The authors conclude that this plant is a satisfactory and economical substitute for *krameria*.

T. J. W.

Peru Balsam and its Adulteration. L. van Itallie. (*Amer. J. Pharm.*, 1921, **93**, 24-26.)—Peru balsam is frequently adulterated by the addition of benzyl benzoate and other esters resembling the natural balsam in odour and appearance. Such adulteration may be detected by the following tests even when the usual analytical values are normal: (1) One drop of the balsam is heated with 0.1 gm. of resorcinol and ten drops of sulphuric acid, cooled, diluted with water, and treated with excess of sodium hydroxide solution. Genuine samples yield only a weak, green fluorescence, but when adulterated an intense green due to fluorescein is formed; (2) One gm. of balsam is dissolved in ether, the liquid shaken with 2 per cent. sodium hydroxide solution, and the alkaline extract acidified after separation. The precipitated resins are dissolved in ether, and the solution gently poured on to the surface of sulphuric acid, when adulteration is shown by the formation of a green or

blue layer. A commercial sample of *Balsamum peruvianum syntheticum* yielded normal values for the usual constants, but gave positive results with the above tests, whilst the addition of five drops of the sample to 8 c.c. of petroleum spirit produced a white precipitate, and a mixture of 1 vol. of carbon disulphide and 3 vols. of the balsam produced a jelly.

T. J. W.

Remijin, an Inferior Japanese Substitute for Optochin (Ethylhydrocupreine). C. A. Rojahn. (*Ber. Deut. Pharm. Ges.*, 1921, **31**, 37-38.)—Examination of remijin, made by the Sankyo Company, Muromachi, Tokyo, and described as ethylhydrocupreine, gave the following results: It was a light-grey powder insoluble in water, sintering at about 105° C. (optochin, 122° C.), m.-pt. 130 to 140° C. (optochin, 126 to 130° C.); loss on drying, 2.7 per cent.; ash, 0.27 per cent.; ethoxyl, 8.94 per cent., corresponding with 67.5 per cent. of the ethylated base; ethereal extract, 65.41 per cent.; and non-ethylated phenolic base, 30.85 per cent. Remijin hydrochloride, a yellowish-white crystalline powder from the same source, sinters at about 60° C., m.-pt. about 105° C. (optochin hydrochloride, 252 to 254° C.); loss on drying, 2.6 per cent.; ash, 0.33 per cent.; ethoxyl, 7.3 per cent., corresponding with 60.9 per cent. of optochin hydrochloride, and ethereal extract of the product rendered alkaline, 59.4 per cent.; non-ethylated phenolic base, 35.4 per cent. Thus, about one-third of the products consists of hydrocupreine, which differs from ethylhydrocupreine physiologically.

T. H. P.

New Rapid Method for the Estimation of Morphine in Opium and its Preparations. T. Ugarte. (*J. Pharm. Chim.*, 1921, **23**, 129-131.)—One grm. of powdered opium is warmed with 10 c.c. of alcohol (67 per cent.) on a water-bath, the clear liquid decanted through a filter, and the insoluble residue treated three times with 10 c.c. of alcohol. The total filtrate is evaporated to dryness in a dish on the water-bath and heated to 100° C. for fifteen minutes to oxidise and render the resins insoluble; the residue is then extracted successively four times with 5 c.c. of cold water (a flat-ended rod being used to break up the residue), and the liquid filtered and evaporated to dryness. The residue is taken up in 2 c.c. of water saturated with morphine, and 3 c.c. of dilute ammonia saturated with morphine are added (9.1 c.c. of ammonia of sp. gr. 0.925 diluted to 100 c.c.); 10 c.c. of ether are next added, and the liquid agitated so as to form an emulsion two or three times, the rapid evaporation of the ether at this stage lowering the temperature to within 2 to 3 degrees above zero. After the addition of another 20 c.c. of ether, the mixture is shaken and allowed to stand for thirty minutes, when the morphine crystallises in small granules on the bottom and sides of the beaker. The ethereal layer is decanted through counterpoised filters, and the morphine is treated with a further 10 c.c. of ether, transferred to the filter by means of a rubber-tipped rod and a jet of water saturated with morphine and ether, and is finally dried at 100° to 105° C. and weighed. In the case of opium preparations (*e.g.*, tinctures), 10 c.c. are evaporated to dryness and heated at 100° C. for fifteen minutes to oxidise the resins, and then treated as above.

R. G. P.

Identification of Theobromine and Caffeine. M. Malmy. (*J. Pharm. Chim.*, 1921, **23**, 89-91.)—A fresh solution of potassium iodobismuthate gives an orange-coloured precipitate both with theobromine and with caffeine; but with old solutions, owing to partial reduction caused by traces of hydrogen iodide, the theobromine coloration changes to chocolate brown. To identify the two alkaloids, 0.05 gm. are mixed with 10 c.c. of water and 0.5 c.c. of fresh potassium iodobismuthate solution, and 5 drops of 10 per cent. iodine, containing about 1 per cent. hydrogen iodide, are then added. In the case of caffeine a bright-red tint is thus produced, whilst with theobromine a brown coloration, changing to chocolate brown in thirty minutes, occurs.

W. J. W.

Proposed Standard for Goldenseal (*Hydrastis*) Root. (*U.S. Dept. Agric. Bureau of Chemistry Service and Regulatory Announcements*, No. 26, 14.)—As a result of the examination of commercial *Hydrastis* root (in both whole and powdered condition) it is considered that the total ash should not exceed 8 per cent., and that the acid-soluble ash should not exceed 3 per cent.

R. G. P.

Estimation of Hydrastine in *Hydrastis canadensis*. N. Wattiez. (*Chem. Abstracts*, 1921, **15**, 145, from *J. Pharm. Belg.*, 1920, **2**, 817-819.)—The rhizomes are dried at 50° C., and 7.5 grms. of the powder extracted for three hours with 150 grms. of 70 per cent. alcohol under a reflux condenser. The mixture is then shaken, cooled, and filtered, 120 grms. of the filtrate are evaporated to a syrup, and the berberine precipitated by the addition of sulphuric acid to give a total weight of 15 grms. After standing one hour 1 gm. of talc is added, and the mixture filtered. Ten grms. of the filtrate are made alkaline by the addition of ammonia and shaken frequently during thirty minutes with 40 grms. of ether. After separation, 35 grms. of the ethereal solution are washed with water and extracted with 1 per cent. hydrochloric acid until the aqueous extract yields no precipitate with Mayer's reagent. The extracts are mixed, filtered, warmed to remove ether, cooled, treated with 5 per cent. silicotungstic acid solution, and heated to 100° C. After standing twenty-four hours the mixture is filtered, and the precipitate washed with water until free from acid, and dried to constant weight. The weight of dry residue multiplied by 0.534 gives the amount of hydrastine in 3.5 grms. of the powdered rhizome. For the assay of the extract and tincture of hydrastis by this method, 6 grms. and 30 grms. are taken respectively.

T. J. W.

Alkaloids of Japanese Corydalis. Y. Asahina and S. Motigase. (*J. Pharm. Chin.*, 1921, **23**, 142.)—The roots of *Corydalis decumbens* (Pers.) contained non-phenolic bases, including protopine, an alkaloid (m.-pt., 142°) perhaps identical with that isolated from *Dicentra formosa* by G. Heyl; and phenolic bases, including bulbocaprine, and another base (m.-pt., 175° C.).

R. G. P.

Lobinol, a Dermatitant from *Rhus diversiloba* (Poison Oak). J. B. McNair. (*J. Amer. Chem. Soc.*, 1921, **43**, 159-164.)—Lobinol is the name suggested for the principal dermatitant of the bark of *Rhus diversiloba*. It is an unsaturated

phenolic compound, and possibly contains two hydroxyl groups in ortho-positions. It absorbs bromine freely, and with ferric chloride its alcoholic solution gives a green and then a black coloration, and afterwards a black precipitate or, if the solution be very dilute, a green coloration turned red on addition of sodium carbonate. It forms an acetyl and a benzoyl derivative, an α -naphthylurethane and a phenyl-carbamate. With Millon's reagent it gives a red coloration, and it reduces silver nitrate on heating and ammoniacal silver nitrate in the cold. It hardens at above 96° C. in absence of its enzyme or an oxidising agent, whilst it reacts violently with concentrated nitric acid yielding a nitrate. It dissolves in many organic solvents and in concentrated alkali hydroxide solution, and is precipitated from its alcoholic solution by a number of metallic salts; with barium hydroxide it gives a green precipitate.

T. H. P.

Substitution of the Fruits of *Piper ribesoides* for Cubebs. (U.S.

Dept. Agric. Bureau of Chemistry Service and Regulatory Announcements, No. 26, 13-14.)—The fruits of *Piper ribesoides* Wallr. have been substituted for cubebs (*P. cubeba*, L.). True cubebs are 3 to 6 mm. in diameter, with stem-like extensions 5 to 7 mm. in length, and give a crimson-red coloration with concentrated sulphuric acid. The fruits of *P. ribesoides* are 5 to 8 mm. in diameter, with somewhat flattened and curved stem-like extensions up to 13 mm. in length, and give a brownish coloration with sulphuric acid. The stone-cells of the inner layer of the fruit-coat of *P. cubeba* are radially elongated, while those of *P. ribesoides* are generally isodiametric. To conform to pharmacopœial requirements cubebs must not contain more than 5 per cent. of stems or other foreign matter; the Department will recommend the exclusion of cubebs containing over 5 per cent. of foreign matter (including fruits of *P. ribesoides*), except where "definite evidence is furnished that the product will be and is used by a manufacturing firm for a purpose which in no way implies that it is the pharmacopœial article."

R. G. P.

Substitution of Flowers of *Onoperdon* Species for Saffron. (U.S.

Dept. Agric. Bureau of Chemistry Service and Regulatory Announcements, No. 26, 14.)—The flower-tops (corolla, stigmas, and anthers) of the "cotton" or "Scotch thistle" (*Onoperdon* sp.) dyed with tartrazine or commercial Ponceau 2. R., and weighted with borax, potassium nitrate and glycerin have been substituted for saffron (*Crocus sativa* L.). Saffron has a tri-lobed stigma, does not contain anthers or corollas, and imparts a characteristic coloration to water (1 to 100,000, or greater dilution). *Onoperdon* has tubular florets (which are much longer than the stigmas of saffron), stamens which show a narrow extension above the anthers, corollas with club-shaped multicellular glandular hairs, and pollen with a peculiar thickened triangular coat. Artificial dyes can be detected by the pink or red coloration with organic solvents, and added salts by the high total ash.

R. G. P.

Examination of Neo-Salvarsan. L. van Itallie. (*Pharm. Weekblad*, 1921, 58, 186-192.)—Neo-salvarsan is an oxidation product of salvarsan, obtained by treatment with sodium formaldehyde sulphonate: $C_{12}H_{11}O_2As_2N_2-CH_2O.SONa$; the com-

mercial substance contains 20 per cent. of arsenic. It may be identified by Denigès-Labot's two reactions: (1) One drop of ferric chloride added to 5 c.c. of neo-salvarsan solution (1 : 1000) gives a red or reddish-violet coloration, which is not destroyed by hydrochloric acid; (2) 0.5 c.c. of hydrogen peroxide, 0.5 c.c. of ammonia, and 1 drop of 4 per cent. copper sulphate solution give with 5 c.c. of neo-salvarsan solution (1 : 1000) an intense bluish-green coloration, changing to red on addition of hydrochloric acid. Arsenic may be detected by Utz's methods (*Pharm. Zentralhalle*, 1920, 4), but hydrogen peroxide may be substituted for sulphuric acid and ammonium persulphate. The neo-salvarsan (0.05 gm.) is dissolved in 0.5 c.c. of hydrogen peroxide, a crystal of ferrous sulphate added, and the solution is gently heated over a flame till evolution of gas ceases. On adding 3 c.c. of Bettendorf's solution and warming, arsenic separates. Lehmann's method (*Pharm. Zentralhalle*, 1913, 725) may be used for the quantitative estimation.

W. J. W.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Study of Molluscs of the Pacific Coast. P. G. Albrecht. (*J. Biol. Chem.*, 1921, 45, 395-405.)—Five species of molluscs were examined, two of these, *Abalone* and the Pismo clam, being of importance in human dietary. The digestive juices both of the stomach and intestines in each of the species showed an acid reaction and contained a variety of enzymes, although cytase was absent from all. Analyses of the muscle tissues showed a high percentage of ash in all species, whilst the protein content varied from 23 per cent. in *Abalone* to 10.26 per cent. in the Pismo clam. Hydrolysis of the alcoholic extract yielded from 5.26 to 27.2 per cent. of reducing sugars calculated on the dry extract. Creatine and creatinine were identified in *Abalone* muscle, these bases not having been previously recorded in molluscan tissues. Amylase and glycogenase were detected in *Cryptochiton* muscle, and urease in that of the Pismo clam.

T. J. W.

Coffee Bean (*Daubentonia longifolia*) as a Poisonous Plant. C. D. Marsh and A. B. Clawson. (*J. Agric. Research*, 1920, 20, 507-513.)—This plant, sometimes named *Sesbania cavamillesii*, is a shrub belonging to the order *Leguminosae*, and occurs in the wild state over an area extending from Florida to Texas. In feeding experiments on sheep the smallest dose of the whole plant producing symptoms of poisoning was 0.066 lb. per cwt. of animal, and the minimum fatal dose was 0.11 lb. The seeds are more highly toxic than the leaves and seed pods, although the roasted seeds have been used as a substitute for coffee without deleterious effect. Various closely related plants have from time to time been described as poisonous. The toxic substance in the plant is excreted very slowly by animals, and poisoning may result from the repeated administration of quantities below the toxic dose. The plant is poisonous to sheep, and probably goats, but no data are extant with regard to its effect upon cattle and horses.

T. J. W.

Use of Chloropierin in the Disinfection of Cereals. A. Piutti and A. Mango. (*Giorn. Chim. Ind. Appl.*, 1920, 2, 677-682.)—Chloropierin, applied in

the proportion of 20 c.c. per cu. m. of grain store and allowed to act for at least a week at a temperature not lower than 15° C., serves as an efficient parasiticide. It produces no tangible effect on the properties either of the grain or of the flour or bread made therefrom, but it lowers the percentage of germinating corns by about one-third.

T. H. P.

Nutritional Requirements of Yeast. I. Rôle of Vitamins in the Growth of Yeast. E. I. Fulmer, V. E. Nelson, and F. F. Sherwood. (*J. Amer. Chem. Soc.*, 1921, **43**, 186-191.)—The results of the authors' experiments on the stimulation of the growth of yeast by extracts of various materials show that the vitamin water-soluble B is not a necessary constituent of a medium for the growth of yeast, since treatment with alkali does not impair the effects of wheat embryo or alfalfa extracts in this direction. These extracts are found to contain nitrogenous and inorganic materials sufficient to maintain the development of yeast. Any method which utilises the stimulating power of extracts upon the growth of yeast as a quantitative method will yield conflicting results.

T. H. P.

Estimation of Bile Acids. C. L. A. Schmidt and A. E. Dart. (*J. Biol. Chem.*, 1921, **45**, 415-421.)—A mixture of 10 c.c. of bile and 8.5 c.c. of alcohol is heated almost to boiling, filtered, and the residue washed with small quantities of alcohol until the cold filtrate measures 100 c.c. Two 20 c.c. portions are evaporated to dryness in porcelain dishes and the remaining 60 c.c. in a nickel crucible, the residue fused with sodium carbonate and sodium peroxide, and the sulphur estimated as barium sulphate. One of the 20 c.c. residues is dissolved in water, diluted to 10 c.c. and 2 c.c. portions used for the estimation of amino nitrogen by the Van Slyke method (*J. Biol. Chem.*, 1911, **9**, 185). The remaining 20 c.c. of residue are washed into a 10 c.c. flask with 8 per cent. sodium hydroxide, heated to 100° C. for eight hours, cooled, diluted to 10 c.c., and the amino nitrogen estimated in 2 c.c. portions. The difference between the results obtained in the two nitrogen estimations gives the taurine and glycocoll nitrogen of the bile acids. The taurine nitrogen is calculated from the sulphur estimation, and the difference between the amino nitrogen due to bile acids and the taurine nitrogen, less 3 per cent., gives the glycocoll nitrogen. The total maximum error is less than 6 per cent., and the results agree with those of other workers obtained by more lengthy methods.

T. J. W.

Removal of Ammonia from Urine. G. E. Youngberg. (*J. Biol. Chem.*, 1921, **45**, 391-394.)—Five c.c. of urine are diluted to 50 c.c., and 20 to 25 c.c. of the dilute solution are shaken with 3 to 4 grms. of dry permutit for five minutes. After settling, the solution is filtered, and the filtrate, which will then be entirely free from ammonia, may be used for the estimation of urea. Tabulated results given show that the accuracy of the urea estimation is unaffected when the original urine contains excess of ammonia or mineral and urinary salts.

T. J. W.

Estimation of Chlorine in Tissues. R. D. Bell and E. A. Doisy. (*J. Biol. Chem.*, 1921, **45**, 427-435.)—The tissue is heated with about four times its weight of

sulphuric acid, ammonium or potassium persulphate being added at intervals until the solution is colourless. The gaseous products of the reaction pass through absorption tubes containing 20 per cent. sodium hydroxide and 10 per cent. sodium carbonate solutions. On completion of the digestion the absorption tubes are rinsed into a flask, slightly acidified, and gently boiled to remove sulphur dioxide and carbon dioxide, when excess of silver nitrate is added, the solution evaporated and centrifuged. The excess of silver is estimated by titration against potassium iodide, using the Van Slyke-Donleavy method (*J. Biol. Chem.*, 1919, **37**, 551). The results obtained are in good agreement with those obtained by Foster's modification of the McLean and Van Slyke method (*J. Biol. Chem.*, 1917, **31**, 483). T. J. W.

Estimation of Sodium in Blood. E. A. Doisy and R. D. Bell. (*J. Biol. Chem.*, 1921, **45**, 313-323.)—Five c.c. of whole blood or plasma are mixed with 35 c.c. of water and treated with 5 c.c. of 20 per cent. trichloroacetic acid, the whole being diluted to 50 c.c. mixed, and filtered after thirty minutes. To 10 c.c. of the filtrate one drop of concentrated nitric acid is added, and the flask heated over an asbestos sheet until brown fumes are evolved, when the contents are cooled. The precipitating reagent is prepared by dissolving 30 grms. of potassium nitrite (free from sodium) in about 60 c.c. of water, adding 5 c.c. of a 60 per cent. bismuth nitrate solution in 2*N*-nitric acid, dissolving any precipitate in dilute nitric acid, and finally running in a strong solution containing 1.6 grms. of caesium nitrate and 1 c.c. of 2*N*-nitric acid, and diluting the solution to 100 c.c. After standing for twenty-four hours, it is filtered and kept at a low temperature in an atmosphere of coal-gas or hydrogen. The solution containing the sodium is cooled to 10° C. and 3 c.c. of the reagent are added for each mgrm. of sodium expected; coal gas freed from sulphuretted hydrogen is employed to displace the air in the flask, and precipitation is allowed to proceed at 1° C. for twenty-four hours. The precipitate is rapidly filtered through a Gooch crucible, washed with a cold 50 per cent. acetone solution saturated with caesium bismuth nitrate, and finally with pure acetone, after which it is dried at 100° C. to constant weight. The weight of precipitate multiplied by the factor 0.03675 gives the sodium. Since this gravimetric method is liable to certain errors the result may be checked by transferring the precipitate, after drying and weighing, into an excess of standard potassium permanganate solution, adding 10 c.c. of 50 per cent. sulphuric acid, heating the liquid to 75° C., running in excess of standard oxalic acid solution, and finally titrating the excess with standard potassium permanganate solution, when mgrms. of oxygen used multiplied by 0.28738 gives the weight of sodium in mgrms. A further modification is described in which the nitrite present in the precipitate is estimated colorimetrically by the Illosvay reagent. The results given for the sodium content of blood and urine agree well with those obtained by the usual indirect method, but are less satisfactory when the gravimetric method is adopted.

T. J. W.

Elimination and Fixation of Therapeutic Novarsenicals. Kohn-Abrest, Sicard, and Paraf. (*Comptes rend.*, 1921, **172**, 301-304.)—In the investigation of arsenic in the human body, the presence of about 1 mgrm. of arsenic in the whole

of the viscera may be disregarded. Amounts between 1 and 3 mgrms. indicate therapeutic arsenical treatment, and are usually found in the liver, kidneys, and intestines. The presence in the viscera of 3 to 7 mgrms. is also compatible with novarsenobenzene treatment occurring two to twenty-five days previously, the substance undergoing normal elimination. When, however, the viscera contain mgrms. of arsenic, arsenical poisoning is indicated.

T. H. P.

WATER ANALYSIS.

Occurrence of Hydrogen Sulphide in Waters at Great Depths. O. Luning. (*Zeitsch. Unters. Nahr. Genussm.*, 1921, **41**, 29-31.)—Hydrogen sulphide is known to be present in the lower layers of sea and lake waters, the quantity increasing with the depth, although none is found in the surface layers. For instance, in the Black Sea, at a depth of 213 metres the water contains 9.0 mgrms. of hydrogen sulphide per litre, whilst at 2,528 metres the quantity increases to 9.98 mgrms. The author has recently met with an instance where a deep but sluggish river contained large quantities of hydrogen sulphide in its lower layers.

W. P. S.

Estimation of Sulphuric Acid in Water. L. W. Winkler. (*Zeitsch. angew. Chem.*, 1920, **33**, 311-312.)—Approximately correct results may be obtained by a rapid nephelometric method of estimating sulphate in water. Five c.c. of the clear water are acidified with 2.5 c.c. of 10 per cent. hydrochloric acid, and treated with 2.5 c.c. of a 10 per cent. solution of barium chloride, and a note taken of the time required for the liquid to become turbid. The amount of sulphuric acid corresponding with the observed time is then obtained by reference to a table or curve, which is preferably constructed from the results given by a standard scale of samples containing known quantities (in mgrms.) of sulphuric acid under the conditions of observation. The results obtained by a gravimetric estimation are inaccurate unless calcium be first precipitated by adding 0.5 to 1.0 gm. of sodium hydroxide and 1 to 2 grms. of sodium carbonate per litre. After the precipitate has subsided, 1 litre of the clear supernatant liquid is acidified with hydrochloric acid and evaporated to dryness, the residue treated with 25 c.c. of water, the solution freed from silica, and the sulphuric acid precipitated from the filtrate.

AGRICULTURAL ANALYSIS.

Investigation into the Occurrence of Different Kinds of Carbonates in Certain Soils. F. Hardy. (*J. Agric. Sci.*, 1921, **11**, 1-18.)—Examination of the soils on the north-west coastal belt of the Wash shows that two groups of naturally occurring carbonates may be distinguished: (1) Calcitoid carbonates, being various forms of calcium carbonate easily decomposed by weak acids; (2) Dolomitoid carbonates, comprising magnesite, dolomite, siderite, and other minerals requiring strong acid for their decomposition.

Calcitoid carbonates do not affect the normal rate and process of nitrification, but cultural experiments show that dolomitoid carbonates retard nitrification; ferrous iron is the principal inhibiting factor. For the estimation of the calcitoid

and dolomitoid carbonates the acetic acid method of Linck (*cf.* Johannsen's "Manual of Petrographic Methods," 1918) is not satisfactory, owing to complications arising from the difference in fineness of the dolomite in soils, and other factors. The following method, based on experiments on calcite sand and clay, was adopted: Thirty grms. of air-dried soil are ground to pass a sieve of 0.2 mm. mesh; of two 12-grm. portions one is shaken for forty-five minutes with a rotatory motion with 100 c.c. of CO₂-free water at room temperature, and the other similarly shaken with 100 c.c. of $\frac{N}{3}$ acetic acid. Each is then filtered through dry papers, and the residues washed with CO₂-free water, and dried in an air oven at about 30° C. When dry, the percentage of carbonate in each is determined by the method of Amos (*J. Agric. Sci.*, 1905, 1, 322) on 10 grms. (5 grms. if the carbonate content be high). The figure obtained on the water-treated soil is the percentage of total carbonate, and that on the treated soil (reckoned as CaCO₃) is taken as the dolomitoid carbonate. The difference gives the calcitoid carbonate.

Calcitoid carbonate was present in the soils examined to the extent of about twice the content of dolomitoid carbonate; these soils have not been cultivated; continued cultivation of the soil reduces the quantity of the calcitoid carbonate more than that of the dolomitoid variety, and a fair proportion of total carbonate may be present, yet the soil be lacking in the calcitoid, or most useful variety and sourness result. Soils not derived from marine silts do not usually contain dolomitoid carbonates.

H. E. C.

Studies on Soil Reaction. E. A. Fisher. (*J. Agric. Sci.*, 1921, 11, 19-65.)—

I. After reviewing the theories of soil acidity it is shown that the many methods described for its determination yield widely different results, and at best only give empirical information on the quantity of lime required. This is partly due to the past unsatisfactory definitions of soil acidity, which scientifically can only mean the hydrogen ion concentration $[H^+]$ in the soil solution, and which is most conveniently expressed as $-\log [H^+]$ (the reciprocal of $\log [H^+]$). The older titrimetric methods fail because of adsorptive and "buffer" effects which are bound up with the solid phase, so that the reaction of a soil solution is only constant when it is in contact with the solid. Much improvement is, however, effected by the use of the sulphone-phthalein dyes instead of litmus. A critical study of the Hutchinson-Maclennan method (*Chem. News*, 1914, 10, 61, abstr. ANALYST, 1914, 450, and *J. Agric. Sci.*, 1914, 6, 323) shows that the results are from three to twenty times as great as those of the colorimetric method, the higher values occurring with slightly acid soils. This is due to adsorption by soil particles, which is expressed by the equation $y/m = kC^p$, where "y" is the lime absorbed by "m" grms. of soil, "C" the amount of lime in the liquid phase, and "k" and "p" are constants. Study of this equation shows that the lime requirement, which cannot in practice be differentiated from the acidity, as shown by this method, will vary with the size of the particles; the fact that the soil does not adsorb equivalent quantities of different bases is also a source of error. Further it shows that the lime requirement of the soil is the sum of two quantities—(1) the lime required to neutralise soil acids, and (2) the lime actually

adsorbed by the soil complex. It is at present impossible to differentiate between these; different classes of soils give very different adsorption curves on plotting the above equation, so that results are unreliable; they can, however, be rendered comparable by interpolating the results from an experimental curve of $\log y/m$ against $\log C$.

II. Methods of estimating $[H^+]$ or $-\log [H^+]$ are electrometric or colorimetric, the latter really depending on standardisation by the former. The colorimetric method is based on the availability of a number of indicators with a wide range of colour changes from $-\log [H^+] = 1$ to $-\log [H^+] = 10$. *Preparation of the Solutions required.*—Standard Buffer Solutions. (*cf.* Clark and Lubs, *J. Bact.*, 1917, 1, 109-191; *J. Biol. Chem.*, 1916, 25, 479).—M/5 HCl, M/5 KH_2PO_4 , M/5 acid potassium phthalate, M/5 boric acid, M/5 KCl and M/5 NaOH, are all made with conductivity water. Potassium acid phosphate, phthalate, and chloride are recrystallised from conductivity water, and dried at 110° to 120° C.; boric acid is recrystallised and air-dried below 50° C.; sodium hydroxide is purified by a special method, and standardised against the acid potassium phthalate. The following mixtures are made: (A) Phthalate mixtures, giving $-\log [H^+] = 2.2$ to 3.8 ; (B) Phthalate-NaOH mixtures giving $-\log [H^+] = 4.0$ to 6.2 ; (C) KH_2PO_4 -NaOH mixtures giving $-\log [H^+] = 5.8$ to 8.0 , and (D) Boric acid-KCl-NaOH mixtures giving $-\log [H^+] = 7.8$ to 9.8 . These solutions keep for about six weeks if a little calomel be added. The following indicators are used (*cf.* Clark and Lubs, *loc. cit.*) for the ranges of $-\log [H^+]$ named: Thymol-blue, 1.2 to 2.8; brom-phenol-blue, 3.0 to 4.6; methyl-red, 4.4 to 6.0; brom-cresol-purple, 5.2 to 6.8; brom-thymol-blue, 6.0 to 7.6; phenol-red, 6.8 to 8.4; thymol-blue, 8.0 to 9.6. These are used in the form of 1.2 per cent. aqueous solutions of the sodium salts (0.6 per cent. for phenol-red, and 0.1 gm. of methyl-red in 500 c.c. of diluted alcohol). On account of dichromatism the determinations are made in daylight. *Method of Using Colour Standards.*—To 10 c.c. of standard buffer solution are added, in three test tubes 4" by 5/8", four drops of indicator (methyl-red, six drops) and the tube closed with a rubber cap. These are compared with 10 c.c. of the solution the $-\log [H^+]$ value of which is required, by a modification of Walpole's method (*Biochem. J.*, 1910, 207). In the case of soil the solution is prepared as follows: 50 grms. of soil (3 mm. sample) are shaken with 100 c.c. of conductivity water in an end-over-end shaker for half an hour; after allowing the mixture to stand for a few minutes the supernatant liquor is centrifuged at 3,000 revs. per minute for ten minutes, and the colour with the indicator measured as above. Experiment shows that filtration disturbs the results. To determine the lime requirement colorimetrically, varying amounts of $\frac{N}{5}$ barium hydroxide solution are added to mixtures of soil with twice its weight of water and the $-\log [H^+]$ value measured as before; the results are plotted and the amount required to make $-\log [H^+] = 7.07$ interpolated and calculated to CaO. The results are not absolute values, but are comparable from sample to sample. The fineness affects the values of $-\log [H^+]$ obtained; 100 mesh samples give lower results than 3 mm. samples, but the centrifuged liquor is turbid and requires flocculation by addition of calcium acetate, which decreases the observed acidity.

H. E. C.

The Preparation and Fractionation of Humic Acid. V. A. Beckley. (*J. Agric. Sci.*, 1921, 11, 66-68.)—From results of attempted determinations of the methoxy content of carefully prepared humic acid, it is concluded that the humic acid of Ehrenberg and Bahr (*J. für Landw.*, 1913, 61, 427) and Oden, which they considered to be homogeneous and of basicity between three and four, is really a mixture of a tribasic and a tetrabasic acid. The humic acid, which is insoluble in ether and other solvents, is divisible into two parts, both acidic, one soluble and the other insoluble in pyridine. The alcohol-precipitated humus may therefore be further fractionated into Hoppe-Seyler's hylatomelanic acid, which yields melanin and other compounds, and into acids which by pyridine extraction give a soluble and an insoluble humic acid. H. E. C.

The Formation of Humus. V. A. Beckley. (*J. Agric. Sci.*, 1921, 11, 69-77.)—The author confirms Fenton's observation that humus is formed artificially by condensation of ω -hydroxymethyl-furfural. At ordinary temperatures the change takes place very slowly, but on boiling a 12 per cent. hydrochloric acid solution of hydroxymethyl-furfural, humus is rapidly produced together with some furfural. Cane sugar, when boiled with 3 per cent. hydrochloric acid, produces hydroxymethyl-furfural, the colour changing through yellow, red, brown, to black with the production of humus. Experiments with amino-acids and polypeptides also confirm the finding of Maillard that humus results, and it is shown that hydroxymethyl-furfural is the intermediate product. It is probable that the furfural produced from hexoses and hexosans by boiling with hydrochloric acid results from the decomposition of the hydroxymethyl-furfural, and it is unnecessary to postulate the formation of furfural to account for the production of humus. Experiments on rotted straw and on soil confirm the suggestion that humus is produced naturally from carbohydrates by the above changes, and although hydroxymethyl-furfural is unstable and polymerises rapidly to humus, evidence of its presence has been obtained. There is no evidence of the formation of hydroxymethyl-furfural during the decomposition of cellulose by *Spirochæta cytophaga*. H. E. C.

ORGANIC ANALYSIS.

Estimation of Organic Compounds by Oxidation with Chromic Acid. H. Cordebard. (*Ann. Chim. analyt.*, 1921, 3, 40-53.)—Oxidation is carried out by treating the substance with an excess (20 c.c.) of *N*-dichromate solution, adding 20 c.c. of sulphuric acid, and gently boiling the mixture for five minutes at a temperature not above 160° C. After cooling, the liquid is diluted with 100 to 150 c.c. of water and a slight excess of $\frac{N}{10}$ ferrous ammonium sulphate is added and titrated back with $\frac{N}{10}$ dichromate solution. The results obtained with a large number of compounds of different types show that the amount of oxygen required under these conditions is in accordance with theory. Preliminary experiments have also led to the following conclusions: (1) Oxidation takes place normally in the case of substances containing C_2H_5 groups or several CH_3 groups attached to one carbon atom, except where there are groupings in which two atoms of carbon and four atoms of hydrogen only require 2.1 atoms of oxygen for their conversion to acetic acid.

(2) From compounds containing nitrogen united with oxygen nitrogen is evolved, whilst compounds containing amino groups evolve ammonia. (3) In the case of compounds containing metalloids, the latter are converted into the anhydrides of maximum oxygen content. (4) In the case of compounds containing halogens, the latter are liberated and, acting as oxidising agents, spoil the determination.

R. G. P.

Estimation of Arsenic in Organic Compounds. G. R. Robertson. (*J. Amer. Chem. Soc.*, 1921, **43**, 182-185.)—The following method, occupying some two hours, may replace the tedious Carius process. About 0.2 gm. of the organic arsenic compound is treated in a 150 c.c. pyrex Erlenmeyer flask with 5.5 c.c. of concentrated sulphuric acid, and when it is completely wetted or dissolved, 1 c.c. of fuming nitric acid is added and the flask set on a hot plate under a hood; the plate is heated so that water in a similar flask boils actively but not excessively, the actual temperature of the mixture undergoing oxidation being approximately 250° C. In about thirty minutes arsphenamine or any of its intermediates are likely to be oxidised completely, whilst such refractory substances as tolylarsenic acid are partly oxidised and partly charred. In general it is safe after an hour to cool the flask slightly, add to it 10 to 15 drops of fuming nitric acid, and heat for five minutes, by which time the oxidation is complete. After 1 gm. of solid ammonium sulphate has been cautiously added, the vessel is shaken for a few moments until the nitrogen has escaped, allowed to cool to below 100° C., and then cooled under the tap, the clear, colourless mixture being carefully diluted with water to a volume of 60 to 70 c.c. One gm. of potassium iodide and a few scraps of porous tile are added, and the flask, fitted with a simple bulb trap, such as an inverted 25 c.c. flask with a side vent, heated on the same hot plate as before until the volume of the liquid is reduced to 40 c.c. The bulb trap is rinsed into the flask, 0.01*N*-thiosulphate solution is added dropwise until the colour of iodine disappears, and the liquid instantly diluted with cold water to 100–120 c.c. and transferred to a flask containing 50 c.c. of 4*N*-sodium carbonate solution. The residual acid is then slightly over-neutralised with sodium bicarbonate, starch solution being added, and the arsenite titrated with standard iodine solution. If a high degree of accuracy be desired, the sodium bicarbonate may be replaced by a buffer solution of phosphates, which keeps the solution exactly neutral during titration.

T. H. P.

Absorption of Carbon Monoxide by Cuprous Ammonium Carbonate Solutions. W. R. Hainsworth and E. Y. Titus. (*J. Amer. Chem. Soc.*, 1921, **43**, 1-11.)—The capacity of a cuprous ammonium carbonate solution of given cuprous copper content to absorb carbon monoxide depends on the free ammonia content of the solution and on the partial pressure of the carbon monoxide above it, as well as on the concentration of the cuprous copper. The absorption takes place in consequence of the formation in solution of an unstable compound probably containing one mol. of carbon monoxide per gm.-atom of cuprous copper. Cupric copper is reduced to cuprous copper fairly rapidly by carbon monoxide, but the reduction of cuprous copper to metal is much slower. The presence of oxygen in small proportions in gaseous mixtures from which carbon monoxide is to be removed by absorption will prevent the precipitation of copper and increase the absorptive capacity of the

solution. Practically complete removal of carbon monoxide from used cuprous ammonium carbonate solutions may be effected by heating to 75° C. at ordinary pressure in an inert atmosphere, the absorptive capacity being restored unimpaired.

T. H. P.

Estimation of Small Proportions of Carbon Monoxide in Air and in Flue Gases. D. Florentin and H. Vandenberghe (*Comptes rend.*, 1921, 172, 391-393.)

—Two methods for estimating carbon monoxide have been investigated: (1) *The Iodine Pentoxide Method* (cf. Teague, *ANALYST*, 1920, 45, 459).—This method is not specific, since the oxide is reduced by many other gases difficult, if not impossible, to remove. The results obtained show that the commercial iodine pentoxide should be purified by solution in water, slow evaporation on a sand-bath at 150° C., and heating in a current of air at 200 to 210° C. to expel occluded iodine and decompose any iodine tetroxide. The proportion of carbon monoxide in the gas should not exceed 0.1 per cent., since otherwise the iodine may be deposited on the cold parts of the apparatus in fine spangles removable only by prolonged washing. The apparatus should contain no glass wool or asbestos, which fix small proportions of iodine, and there should be no rubber connection between the iodine pentoxide tube and the iodine-absorption vessel. The reaction between carbon monoxide and iodine pentoxide being slow, a U-tube containing a 20 cm. column of the powdered pentoxide at 140° to 150° C. should be used, and the volume of gas passed through it should not exceed 700 to 800 c.c. per hour. (2) *The Blood Method*.—The air is freed from oxygen by shaking it with a concentrated sodium hydroxide solution of sodium hydrosulphite, and is then passed through a 1 per cent. blood or hæmoglobin solution at the rate of about 600 c.c. per hour. The number, N , of c.c. of oxygen-free air required to cause the appearance of the absorption bands of the hæmoglobin-carbon monoxide compound in the spectrum of the blood solution varies with the number of parts, M , of carbon monoxide in 100,000 parts of the original air in accordance with the following table, which it is advisable for the observer to check:

N	90	125	150	200	300	400	500	750	1000	1300	2200
M	100	60.6	45.0	25.0	13.3	8.8	6.5	3.7	3.1	2.0	1.0

If the gas to be analysed contain more than 0.1 per cent. of carbon monoxide, it should be diluted before testing. For the gas from the combustion of different fuels, such as sawdust, lignite, etc., this method gives absolutely constant results, whereas the iodine pentoxide method mostly gives quite erroneous results owing to the presence of various organic substances.

T. H. P.

Application of the Law of Hydrolysis to the Determination of Molecular Weights. H. Colin and A. Chaudun (*Comptes rend.*, 1921, 172, 278-280.)—The course of the enzymic inversion of sucrose is governed by the relation between the concentrations of sugar and enzyme.

With a given quantity, n_1 , of the catalyst, measured by a certain volume of an enzyme solution, there corresponds a definite weight, a_1 , of sucrose. If n_1 c.c. of the enzyme act on a quantity of sucrose not greater than a_1 , the velocity of hydrolysis diminishes throughout the action in accordance with Wilhelmy's law, but if the weight of sugar exceed a_1 , the velocity

remains constant until the excess of sugar has disappeared, and subsequently diminishes until the action is complete. Similar relations are met with if the sucrose be replaced by raffinose, gentianose, etc., from which the levulose residue is detached by invertase. It is, indeed, found that the weights of the different sugars capable of fixing one and the same amount of sucrase are in the ratios of the molecular weights of the sugars. When solutions of various concentrations of sucrose, raffinose, and gentianose were hydrolysed under similar conditions as regards temperature and content of sucrase—the sugar being always in excess with reference to the enzyme—the weights of the three sugars present in the solutions when the velocity of hydrolysis began to decrease were respectively 1.83, 3.18, and 2.69 grms., which are proportional to the molecular weights of the three sugars. T. H. P.

Methylation of Cellulose. III.—Homogeneity of Product and Limit of Methylation. W. S. Denham. (*J. Chem. Soc.*, 1921, 119, 77-81.)—By repeated treatment of cellulose with sodium hydroxide and methyl sulphate a product containing 44.6 per cent. of methoxyl has been obtained, which indicates that the limit of methylation corresponds to the formation of trimethyl-cellulose. The solubility of methylated cellulose in Schweitzer's reagent decreases as the methoxyl content increases; products containing 40 per cent. of methoxyl are nearly homogeneous, and are practically insoluble in Schweitzer's reagent and in alcohol, acetone, or chloroform. Fehling's solution is not reduced by the highly methylated products. H. E. C.

Volumetric Estimation of Mixtures of Acids and of Bases, and of Polybasic Acids or Bases. H. T. Tizard and A. R. Boeree. (*J. Chem. Soc.*, 1921, 119, 132-142.)—The conditions for the accurate titration of mixtures of two weak acids, or bases, present in the ratio of 1 to x equivalents, or for the titration of dibasic acids or bases to the half-way point, are that K_1/xK_2 should be at least 2.5×10^4 , and that an indicator should be available which changes over at $C_H = \sqrt{xK_1K_2}$ (where K_1 and K_2 are the dissociation constants). If K_1/xK_2 be at least 2.5×10^4 an accuracy of 1 per cent. is possible, and if this ratio be 10^6 , an accuracy of 0.1 per cent. is possible. Experiments and the theory show that the following mixtures can be accurately titrated: Ammonia and aniline using cresol-red; ammonia and β -picoline using methyl-orange; phenol and acetic acid using azolitmin or cresol-red; trichloroacetic and acetic acids using methyl-violet. Monochloroacetic acid cannot be titrated in the presence of acetic acid, since K_1/K_2 is too small; similarly, succinic acid cannot be titrated to the half-way point, although maleic acid can be if methyl-orange be used. If the salt of a polybasic acid having very different dissociation constants be used as a hydron regulator, a slight excess will have a large effect; hence an appropriate mixture of ammonia and acetic acid is preferred for this purpose. H. E. C.

Iodoform Reaction. N. Schoorl. (*Pharm. Weekblad*, 1921, 58, 209-210.)—In Kunz's reaction (*ANALYST*, 1920, 45, 458), ammonium persulphate may be used instead of the potassium salt. In the former case the iodoform has an intense

orange colour and is devoid of crystalline structure. The reaction becomes extremely sensitive if acetone be used, and is effective with concentrations of 1 : 100,000. In addition, with acetone instead of alcohol, the reaction may be carried out with 2 *N*-sodium carbonate instead of sodium hydroxide solution.

W. J. W.

Estimation of Oil of Turpentine. H. Salvaterra. (*Chem. Zeit.*, 1921, 45, 133-135, 150-151, 158-159.)—Three suitable methods for the estimation of oil of turpentine are described. In a modification of Tausch's method, 20 c.c. of the sample are introduced into a 2-litre flask containing 300 c.c. of water and 20 c.c. of 80 per cent. acetic acid. Fifty-one grms. of powdered mercuric oxide are slowly added, and then 10 c.c. of methyl alcohol, after which the flask is connected with a reflux condenser and heated on a water-bath for two to three hours. The undecomposed hydrocarbons, present as impurities, are then distilled off in a current of steam and measured. For the examination of oil of turpentine adulterated with benzine 20 c.c. are added to 20 grms. of potassium bromide and 10 c.c. of water. Fifty c.c. of 50 per cent. hydrogen bromide are run in slowly with continuous cooling, after which the temperature is allowed to rise to 40° to 50° C. After standing for one hour, the solution is neutralised, and the bromine is fixed by addition of solid sodium carbonate and powdered arsenic acid until the solution becomes almost colourless. It is then distilled in steam. If solvent naphtha be present, excess of bromine must be avoided. Twenty c.c. of turpentine oil are treated with 12 grms. of sodium bromate and 10 c.c. of water. Hydrogen bromide is then added till the coloration persists for five minutes, the operation being preferably performed with exclusion of daylight. The temperature is then raised to, and maintained at, 20° to 25° C. for half an hour, and the solution is neutralised and distilled in steam as before. When pine oil (*Kienöl*) is present as the adulterant the bromine oxidation may be incomplete, and it is advisable to add 2 c.c. of hydrogen bromide after the coloration has lasted for ten minutes. The method is unsuitable in case of adulteration with tetrahydronaphthalene. In the iodine method 10 c.c. of turpentine oil are introduced into a flask containing 40 grms. of iodide, 52 grms. of mercuric chloride, and 100 c.c. of alcohol, the mixture being kept cool and then allowed to stand in the dark for six hours. A concentrated solution of potassium iodide is then added, and excess of sodium thio-sulphate solution, after which the mixture is neutralised with sodium hydroxide, and finally distilled in steam. By applying both the mercuric acetate method and either the bromine or iodine process, it is possible to estimate the amount of pine oil in the adulterants, as by the first method 10 per cent. of this substance separates in the distillate, which is not the case with either of the other two processes. The difference in the respective separations, multiplied by 10, will give the content of pine oil.

W. J. W.

Estimation of Aromatic Hydrocarbons in Mixtures with Petrol. H. T. Tizard and A. G. Marshall. (*J. Soc. Chem. Ind.*, 1921, 40, 20-25T.)—The method described is developed from the one previously worked out by Thole (*ANALYST*, 1919, 44, 144.)—Ten c.c. of the mixture are added to 10 c.c. of freshly distilled aniline in a

large test tube fitted with a stirrer and a thermometer reading to 0.1° C. The mixture is heated until a clear solution is obtained, when the temperature is allowed to fall slowly until the mixture suddenly becomes turbid, at which point the thermometer is read. This temperature is called the "aniline point." A second portion of the mixed hydrocarbons is shaken with three times its vol. of 98 per cent. sulphuric acid for half an hour, the residue being separated, washed with sodium hydroxide solution and water and dried over calcium chloride, and the "aniline point" again determined. The difference in degrees between the two results represents approximately the percentage by weight of aromatic hydrocarbons in the original mixture, whether consisting of benzene, toluene, or xylene, or mixtures of the three. In the case of mixtures containing two or more aromatic hydrocarbons, the percentage of each may be determined by fractional distillation of the original mixture, and determining the respective "aniline points" of the fractions distilling up to 95° C., from 95° to 122° C., and from 122° to 150° C. Assuming the first fraction to contain all the benzene, the second the whole of the toluene, and the third all the xylene from the original mixture, satisfactory results were obtained with known mixtures. The accuracy of the results may be increased by a determination of the "aniline point" for small fractions obtained close to 95° and 122° C. by a preliminary distillation and plotting a curve of the "aniline points" and mean boiling points of the fractions, when the maxima indicate the most correct "cutting points" for the distillation of the mixture under examination. T. J. W.

Lamp Method of Estimating Sulphur in Petroleum Spirits. J. S. Jackson and A. W. Richardson. (*J. Inst. Petrol. Technol.*, 1921, 7, 25-34.)—In the lamp described, the ordinary wick is replaced by a bundle of capillaries which are spread by means of a central air tube lightly jammed into position. By this arrangement the air does not pass through the spirit to be burnt, so that fractionation is greatly reduced, if not eliminated. A mixing chamber is provided above the tops of the capillaries, and the luminosity and size of the flame are easily controlled by the air supply. Any sulphur held on the capillaries can be washed off, oxidised, and included in the estimation, but the quantity of sulphur thus held is usually negligible. W. P. S.

Laboratory Testing of Oil Shale for Oil and Ammonia Yield. E. L. Lomax and F. G. P. Remfrey. (*J. Inst. Petrol. Technol.*, 1921, 7, 34-47.)—*Oil.*—This is estimated by distillation with steam. The retort used consists of a 20-inch length of 3-inch iron pipe, mounted horizontally and fitted at each end with reducing sockets; the inlet end is connected with a steam supply and the outlet end with a condenser, vessel for receiving the distilled oil, a second condenser, vessels containing oil (these act as gas scrubbers), and an aspirator filled with water (to measure the gas yield). One kilo of the shale is placed in the retort, which is then heated, and steam at 180° C. is admitted slowly; the heat is increased gradually to ensure a steady distillation of oil, and at the end of the operation the retort is heated to dull redness. The crude oil is further examined as to its sp. gr. solidifying point, sulphur content, water content, and fractional distillation. The first fraction, light naphtha,

volatile below 150° C., is distilled directly; steam is then introduced and fractions collected between 150° and 200° C. (heavy naphtha), 200° and 250° C. (light kerosene), 250° and 300° C. (heavy kerosene); the higher boiling oils are then collected in fractions of 5 or 10 per cent. each. The naphtha fractions are refractionated, and the high boiling oils are examined as to their sp. gr., paraffin wax content, etc.

Ammonia.—The retort described above is used, the shale being placed in the middle section of the retort, and the two ends filled with ignited broken fire-brick. The ends of the retort are brought to a dull red heat before the shale is heated; steam at 180° C. is then admitted, and the whole retort heated rapidly to a dull redness. The receiver and absorption vessels contain dilute sulphuric acid, and at the end of the operation their contents are mixed, diluted to a definite volume, and the ammonia estimated in the usual way.

W. P. S.

New Specific Test for Phenol. G. Rodillon. (*J. Pharm. Chim.*, 1921, **23**, 136-137.)—A drop of sodium nitrite solution (10 per cent.) is mixed with about 10 c.c. of the liquid in a test-tube, and a few c.c. of sulphuric acid are added without mixing; in the presence of phenol a ring, which is emerald-green below and ruby-red above, forms at the zone of contact. It is necessary that the phenol should be free from substances producing colorations with sulphuric acid.

R. G. P.

INORGANIC ANALYSIS.

Properties of Selenium Oxychloride. V. Lenher. (*J. Amer. Chem. Soc.*, 1921, **43**, 29-35.)—Selenium oxychloride (m.-pt. 8.5°, b.-pt. 176.4° at 726 mm., n_D^{20} 1.6516, specific electrical conductivity about 9.6×10^{-4} at 28° C.) is pale yellow and transparent to ordinary light, but it makes a practically perfect screen for all wavelengths below 4050. The oxychloride dissolves sulphur, selenium, tellurium, bromine, iodine, and phosphorus, the last violently; boron, silicon, and carbon in its various forms are unattacked in the cold. Most metals react with the oxychloride, giving the chloride of the metal and selenium monochloride. A solution of sulphur trioxide forms a powerful solvent which dissolves the oxides of aluminium, chromium, the rare earth metals, titanium, columbium, molybdenum, vanadium, and uranium, that of tantalum slightly, but not those of zirconium and tungsten. Strontium carbonate dissolves easily and barium carbonate slightly, calcium carbonate being insoluble; in the cold zinc carbonate dissolves at once, but the carbonates of lead, copper, nickel, and cobalt are only slightly attacked, whilst that of magnesium becomes colloidal. Saturated paraffin hydrocarbons are attacked slowly by the oxychloride at a high temperature, whilst unsaturated aliphatic hydrocarbons, as well as turpentine, etc., unite directly and often violently, and aromatic hydrocarbons form mixtures capable of physical resolution; thus such separations as heptane from amylene or from benzene may be effected. Protein-containing materials, such as hair, bristles, silk, and leather, are dissolved in the cold, but cellulose is not attacked. Pure and vulcanised rubber, vulcanite, bækelite and its allies, gums, resins, dried paints, shellac, dried varnish, lacquer, agar-agar, celluloid, gelatin, and glue dissolve in the oxychloride, as do the natural asphalts, resins, and bitumens when they are unsaturated.

T. H. P.

Use of Gallium Ferrocyanide in Analysis. L. E. Porter and P. E. Browning. (*J. Amer. Chem. Soc.*, 1921, **43**, 111-114.)—When separated as ferrocyanide gallium forms a gelatinous precipitate difficult to filter. It is found that if a mat of fine filter-paper fibre, best made by scratching some paper with a knife, be washed into the funnel containing a double filter-paper, the gallium ferrocyanide is retained provided that the suction used be not too strong; the first portion of the filtrate may have to be returned to the filter. Direct ignition of the ferrocyanide and subsequent weighing of the mixed gallium and ferric oxides yield high results. If, however, the gallium ferrocyanide be treated with an alkali hydroxide solution and carbon dioxide passed through the liquid to saturation, the gallium is precipitated quantitatively as hydroxide or basic carbonate in a form easy to filter and to wash free from ferrocyanide; the precipitate is ignited and weighed as Ga_2O_3 . Another method which works well and is rather quicker than the carbon dioxide method consists in oxidising the gallium ferrocyanide to ferricyanide by hydrogen peroxide in alkaline solution and boiling the solution with ammonium chloride, gallium hydroxide free from cyanide radicles being thus precipitated. This procedure cannot be followed if zinc be present, owing to the insolubility of zinc ferricyanide in acid and in ammonium hydroxide. In this case, either (1) the mixed ferrocyanides are dissolved in sodium hydroxide solution, the bases precipitated together by means of carbon dioxide, and the gallium separated from the zinc by dissolving the precipitate in hydrochloric acid and boiling the solution with acid ammonium sulphite to precipitate the gallium; or (2) the alkaline solution of the ferrocyanides is treated with hydrogen sulphide to precipitate the zinc, the zinc sulphide filtered off, and the gallium recovered from the filtrate free from ferrocyanide either by precipitation with carbon dioxide or by boiling with ammonium chloride after oxidation of the excess of sulphide and of the ferrocyanide by means of hydrogen peroxide.

T. H. P.

Separation of Gallium from Indium and Zinc by Fractional Crystallisation of the Cæsium Gallium Alum. P. E. Browning and L. E. Porter. (*J. Amer. Chem. Soc.*, 1921, **43**, 126.)—The separation of gallium and indium by the fractional crystallisation of the cæsium sulphate alums of these elements (*cf.* Uhler and Browning, *Amer. J. Sci.*, 1916, **42**, 389) has been further studied to determine quantitatively the progress of the separation. A mixture containing 26.5 parts of gallium oxide to 73.5 parts of indium oxide was converted into the cæsium alums; fractional crystallisation of the latter yielding successive fractions containing respectively 100.0, 95.3, 64.3, 23.4, 1.9, and 0.6 (mother liquor) per cent. of gallium oxide in the total oxide present. Gallium may be freed from zinc in a similar manner.

T. H. P.

Qualitative Separation and Detection of Uranium, Vanadium, and Chromium when Present together. P. E. Browning. (*J. Amer. Chem. Soc.*, 1921, **43**, 114-115.)—The author modifies the method given by Noyes (*J. Amer. Chem. Soc.*, 1908, **30**, 481) for separating uranium, vanadium, and chromium, the introduction and subsequent removal of lead being avoided. The solution containing

chromic and vanadic acids, together with a uranium salt, is made faintly alkaline with ammonia and then faintly acid with acetic acid, and treated with ammonium phosphate. The uranium phosphate thus precipitated is filtered off and washed, the filtration being facilitated, if necessary, by addition of shredded filter-paper. The precipitate is treated on the filter-paper with acidified potassium ferrocyanide solution, a characteristic reddish-brown stain resulting if uranium be present. The filtrate is treated with a distinct excess of sulphurous acid, which reduces the chromic and vanadic acids, the solution being successively boiled to remove the excess of sulphurous acid, treated with distinct excess of bromine water, and boiled to expel the excess of bromine. The bromine oxidises the vanadium to the acid condition, but does not affect the reduced chromium. While the excess of bromine is being boiled away some of the chromium is precipitated as phosphate, and this precipitation may be rendered complete by adding ammonia in slight excess and boiling off the excess; a green precipitate indicates chromium. After removal of the chromium by filtration the filtrate is made alkaline with ammonia and saturated with hydrogen sulphide, which gives the pink or violet oxysulphide of vanadium if the latter be present.

T. H. P.

Volumetric Determination of Iron by Means of Titanous Salts. W. M. Thornton, jnr., and J. E. Chapman. (*J. Amer. Chem. Soc.*, 1921, **43**, 91-102.)—The conditions under which Knecht and Hibbert's method (*Ber.*, 1903, **36**, 1549) may be employed have been examined. The replacement of the bead valve of the original apparatus by a three-way cock is recommended. Titanous sulphate was used instead of the chloride, since it gives a solution which appears to maintain its strength indefinitely. Although many objections have been raised against ferrous ammonium sulphate as an oxidimetric standard, it is found that this salt, if of good quality, serves as a sufficiently accurate standard for titanous solutions, since only the total iron content is of importance in this case. Where there is no special objection, 10 c.c. of 10 per cent. ammonium thiocyanate solution is a safe and ample quantity of indicator, and in no case should there be present less than 2.5 c.c. of such solution. The influence of certain acids and of other interfering substances, the preliminary oxidation for the determination of total iron, the direct determination of ferric iron, the verification of the iron determinations, and the determination of iron and available oxygen in artificial manganese dioxide, are among the other questions considered.

T. H. P.

Reaction of Manganese Salts. V. Maeri. (*Ann. Chim. analyt.*, 1921, **3**, 55-56.)—On adding a few drops of a solution of an alkali oxalate and of acetic acid to an alkaline solution of a manganese salt, a rose-red coloration is produced. The reaction is more sensitive if the solution of manganese salt be boiled before the addition of oxalate and acetic acid, and does not occur in presence of strong mineral acid. A definite coloration is obtained with one drop of a 1 : 1000 manganese solution. Phosphoric acid appears to possess the same action as oxalic acid.

R. G. P.

Interference of Phosphates with Detection of Manganese. T. Sabalitschka' and H. Niesemann. (*Ber. Deut. Pharm. Ges.*, 1921, **31**, 30-36.)—The method given by Schmidt ("Anleitung zur qualitativen Analyse") for the detection of

manganese fails in presence of a large proportion of barium or strontium phosphate, but the following modification yields satisfactory results: The precipitate formed by ammonium sulphide is washed with water containing ammonium sulphide and dissolved in cold 5 per cent. hydrochloric acid solution, the solution being filtered and a small portion of the filtrate tested for iron and phosphoric acid. If the latter be found, the acid solution is evaporated with 2-3 grms. of concentrated sulphuric acid, 2-3 grms. of saturated potassium sulphate solution, and, if iron be present, a little nitric acid, until dense white fumes are evolved. The mixture of sulphates thus obtained is treated with alcohol, the undissolved residue being taken up in a little boiling dilute hydrochloric acid, and filtered from the insoluble sulphates of barium, strontium, and calcium. The filtrate is treated with ammonia solution, and the precipitated aluminium, iron, and chromium hydroxides removed by filtration. To the filtrate are added 3-5 grms. of ammonium chloride and also ammonium sulphide, the precipitated manganese and zinc sulphides being dissolved on the filter in a little dilute hydrochloric acid and the solution thus obtained heated to expel hydrogen sulphide, treated with excess of sodium hydroxide solution, and tested for manganese and tin. The filtrate from the sulphide precipitate, which may contain calcium and magnesium, is evaporated to dryness, the residue being heated to expel ammonium salts, moistened with hydrochloric acid, and dissolved in water; the filtered solution is treated with ammonia solution in excess, and tested for calcium and magnesium. The above procedure admits of the detection of 0.05 gm. of zinc oxide and 0.05 gm. of crystallised manganese chloride in the mixture. In presence of smaller amounts of zinc and manganese, the amounts of these metals in the alcoholic extract must also be considered, the process then requiring some further modification.

T. H. P.

Iodimetric Titration of Chromium. J. M. Kolthoff. (*Zeitsch. anal. Chem.*, 1920, **59**, 401-415.)—Zulkowsky's method gives good results if the acid concentration be not below 20 per cent. 4 *N*; and direct titration may be carried out. The concentration of the iodine and dichromate is of small importance. Presence of molybdate retards reaction between iodine and chromium, and further promotes by-reactions between the chromium and thiosulphate, especially in sunlight. Ferrous salts exert a positive catalytic effect in weak acid solution, but with strong acid solutions the interaction of the iodine and chromium salt is impeded. The reaction velocity is not affected by temperature. Even dilute dichromate solutions may be satisfactorily titrated; dilution of the solution after adding the reagents is unnecessary.

W. J. W.

Acidimetry of Boric Acid. J. A. M. v. Liempt. (*Rec. Trav. Chim. Pays-Bas*, 1920, **39**, 358-370.)—The author investigates electrometrically the method based on the addition of polyhydric alcohol to the solution of boric acid previous to titration. The hydrogen ion concentration is plotted against the volume of alkali added, in presence of various quantities of mannitol, glycerol, or lævulose, and if sufficient of the alcohol be present the curves show a marked inflection at the neutralisation point. Curves for mixtures of acetic and boric acids and for borax are included.

O. E. M.

Solid Lubricants.* (*Dept. Scientific and Ind. Research. Bull. No. 4, 1920, pp. 28.*)—A description is given of the characteristics of solid materials used for lubricating purposes, of the action of solid lubricants, their analysis, methods of application and drawbacks, and of the results obtained by their use in practice. The following analyses by L. Archbutt show the composition of various commercial lubricating graphites calculated on the dry material free from volatile matter :

	Acheson Graphite. No. 1,340.	Graphite from "Aquadag."	Graphite from "Oildag."	"Foliac." No. 100.	"Graphite." B. 1,371.	"Foliac." No. 2.	"Foliac." No. 1.	"Foliac." No. 101.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Graphite	99·34	98·68	97·58	99·62	93·74	98·06	90·06	99·95
Mineral matter (ash) ...	0·66	1·32	2·42	0·38	6·26	1·94	9·94	0·05

The "aquadag" contained 15·06 per cent. of material insoluble in water after coagulation by slight acidification, and the "oildag" containing 11·2 per cent. of graphite, etc., insoluble in ether. In the Acheson graphites the principal impurities were iron and alumina, whilst in the "foliac" natural graphites silica (1·60 to 4·40 per cent. of the ash) was the main impurity. "Foliac" graphite No. 100 was nearly chemically pure, the flakes appearing absolutely black when not reflecting light.

PHYSICAL METHODS, APPARATUS, ETC.

Use of Phosphoric Acid instead of Sulphuric Acid in Melting-Point Determinations. A. Graustein. (*J. Amer. Chem. Soc.*, 1921, **43**, 212-213.)—Phosphoric acid, prepared by heating orthophosphoric acid to the highest temperature desired, in order to obtain the necessary concentration, is recommended in place of sulphuric acid in melting-point baths. A vessel of resistance glass, such as pyrex, must be used. Clouding of the acid is removed by adding water and reheating, and discoloration by introduction of a few crystals of sodium nitrite. T. H. P.

Temperature as a Function of the Absolute Viscosity of Oils and other Liquids. H. Schwedhelm. (*Chem. Zeit.*, 1921, **45**, 41-42.)—The absolute viscosity of an oil, calculated from the Engler viscosity, is related to the temperature as shown by the equation: $\frac{z}{G} = \left(\frac{z'}{G}\right) (H^{t-t'})$, in which z and z' are absolute viscosity at temperatures t and t' , whilst G and H are constants, a table of which is given for a number of oils. In the case of mineral lubricating oils, G varies from 0·01887 to 0·02357, and H from 1·01485 to 1·01858; with rape oil, $G = 0·01887$ and $H = 1·01218$; with water, $G = 0·00145$ and $H = 1·01278$; and with alcohol, $G = 0·000160$ and $H = 1·00441$. The equation permits values to be calculated where experimental determination—at high or low temperatures—is difficult. O. E. M.

* By permission of H.M. Stationery Office.

Fractional Precipitation. P. Jolibois, R. Bossuet, and Chevry. (*Comptes rend.*, 1921, 172, 373-375.)—The apparatus previously designed for the systematic study of consecutive precipitation in a chemical reaction (*ANALYST*, 1920, 45, 65) is now applied to the investigation of fractional precipitation. Use is made of two dilute solutions, *A* and *B*, which give a precipitate when mixed, the titre of *A* being constant, whilst that of *B* is varied in different experiments and so calculated that a certain known fraction of the substance is precipitated. The compositions of the liquid and the precipitate indicate the fractionation effected. By this means it is shown that addition of sodium hydroxide solution to a mixture of equal volumes of $\frac{N}{20}$ cupric nitrate and silver nitrate results in the complete precipitation of the copper before any silver is precipitated. With a mixture of $\frac{N}{80}$ solutions of nickel and cobalt chlorides, however, the fractionation effected by precipitation with sodium hydroxide solution is imperfect. The precipitate is always richer in nickel than would be the case if the two metals were equally precipitated, and the content of cobalt in the supernatant liquid increases with the content of sodium hydroxide in the precipitating solution. It is probable that basic salts are formed during this precipitation, since the quantities of metal remaining in the liquid decrease almost proportionally to the quantity of sodium hydroxide introduced.

T. H. P.

Conductimetric Titration. A. Heldring. (*Chem. Weekblad*, 1921, 18, 96-97.)—The conductimetric estimation of organic acids, involving decomposition of their salts in suspension in a mixture of alcohol and water by means of strong acids, may be simplified in various ways. Stirring of the liquid in the thermostat may be more conveniently effected by compressed air than by mechanical means; the air may be previously heated if desired. Removal of the electrolyte vessel and electrodes for the purpose of shaking by hand after addition of acid is also obviated by employing air agitation; to avoid loss of alcohol, it is advisable to pass the air first through a mixture of alcohol and water. Several estimations may be carried out in the same thermostat by the use of connectors. To secure more rapid equilibrium in the alcoholic liquid by increasing the temperature in the thermostat, it is necessary to substitute higher alcohols, also miscible with water, for ethyl alcohol.

W. J. W.

Critical Temperature of Solution and Turbidity-Temperature of Hydrocarbons, etc. N. Chereheffsky. (*Ann. Chim. analyt.*, 1921, 3, 53-55.)—The following solvents are recommended for use in the determination of the critical temperature of solution: (*a*) For petroleum spirit, paraffin lamp oil, lubricating oil, vaseline, ceresine and paraffin waxes—ethyl alcohol, 96.5 per cent.; (*b*) for turpentine oils—ethyl alcohol, 90 per cent.; and (*c*) for castor oil—ethyl alcohol, 85 per cent. And for the determination of turbidity temperature: (*a*) For petroleum spirit and paraffin lamp oils—acetic anhydride; (*b*) for lubricating oils—equal volumes of glacial acetic acid and toluene; (*c*) for vaseline—amyl alcohol, 129° to 131°; (*d*) ceresine and paraffin waxes—crystallisable benzene; and (*e*) for oleines and unsaponifiable matter—aniline and glacial acetic acid.

R. G. P.

An Improved Pyknometer. R. Saar. (*Chem. Zeit.*, 1921, 45, 102-104.)

—To simplify calculation, the pyknometer, which is only suitable for liquids of specific gravity approximating to unity, has a narrow neck with divisions corresponding to mgrms. of water, 150 above and 150 below the mark indicating the nominal content. The instrument being charged and its temperature brought to 15° C., the level and weight of the liquid are ascertained. The number of mgrms. above the normal mark is subtracted from, or the number below added to, the net weight of the liquid.

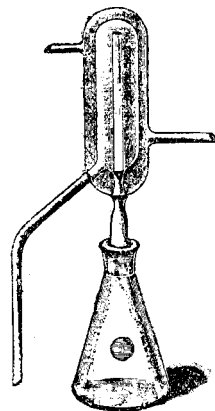
O. E. M.

Soxhlet Apparatus. L. Soep. (*Chem. Weekblad*, 1921, 18, 97.)—The lateral vapour tube enters the upper portion of a Soxhlet apparatus near the base, and is then continued upwards in the form of a spiral surrounding the extraction thimble. By this arrangement the solvent vapours serve to heat the condensed liquid.

W. J. W.

Distillation Apparatus for Small Quantities. C. Woytacek. (*Chem. Zeit.*, 1921, 45, 82.)—The apparatus consists of a 100 c.c. conical distilling flask with ground-in condenser of the form shown.

O. E. M.

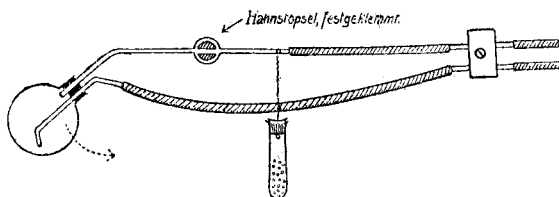


Glass Autoclave. Schmidt. (*Chem. Zeit.*, 1921, 45, 131.)—For reactions in which appreciable evolution of gas takes place, or in which the introduction of gas under pressure is desired, a glass autoclave may be employed. The apparatus includes two condensers, and is provided with an inlet tube for the gas and an outlet tube connected with a safety-valve. It may be employed with pressures up to 4 atmospheres.

W. J. W.

Non-return Arrangement for Water Pumps. H. Dorsch. (*Chem. Zeit.*, 1921, 45, 32.)—A narrow-bore glass cock is connected at one end by a length of pressure tubing with the apparatus to be exhausted, and at the other end carries a small flask. The arrangement is free to rotate around the plug of the cock, held in a clamp, as fulcrum. By means of pressure-tubing the flask is connected with the pump, and receives any water flowing back from the same, the weight of which depresses it until the cock is shut. When the action of the pump improves, the water is drawn off, the flask is raised by a counterweight, and the cock is opened.

O. E. M.



Improved Soxhlet Apparatus. O. Hagen. (*Chem. Zeit.*, 1921, 45, 19.)—To facilitate removal of samples during an extraction the tube connecting the boiling-flask and the apparatus is bent into a ring which is provided with a draw-off cock at its highest point. A funnel directs the condensed solvent into the centre of the extraction thimble.
O. E. M.

Repair of Crystallised Glass Apparatus. A. F. O. Germann. (*J. Amer. Chem. Soc.*, 1921, 43, 11-14.)—In the devitrification of glass the silica which separates forms an infusible coating over the surface of the glass, and may under certain conditions dissolve in the underlying silicate, so that the surface clears up, whilst under other conditions it yields calcium silicate, fusing with difficulty; in which case well-defined crystal surfaces may appear. According to the older hypothesis, this phenomenon is due to slow volatilisation of sodium oxide from glass near its softening temperature, and a common practice has been to reintroduce the lost alkali; this is, however, always difficult. It is found that the tendency to devitrify may be removed by rinsing the parts of the glass to be fused with dilute hydrofluoric acid; this treatment renders possible the repair of old apparatus.
T. H. P.



REVIEWS.

A SYSTEM OF PHYSICAL CHEMISTRY. Vol. II.: THERMODYNAMICS. Third Edition
By W. C. McC. LEWIS, M.A. (R.U.I.), D.Sc. London: Longmans, Green
and Co. Price 15s. net.

Professor Lewis's work is sufficiently well known as a standard textbook of physical chemistry to require but little description. The third edition of Volume II., in which the facts of physical chemistry are treated from the standpoint of thermodynamics, contains a few additions in the light of recent work, notably an extensive new section in Chapter VIII., dealing with the advances made by the American school of physical chemistry on solutions of electrolytes and ionic activity. In Chapter XI. the section on Donnan's Theory of Membrane Equilibria is enlarged, and in the same chapter is an entirely new section, giving a comprehensive account of the Micelle Theory of Colloidal Electrolytes. In the treatment of both of these subjects considerable space has been given to experimental details; such descriptions form a relieving break in a volume, the pages of which are, of necessity, mainly mathematical.

Chapter VII. also contains some additions dealing with advances made in the field of electrochemistry. A recapitulation of the contents of a few of the chapters serves to give an idea of the scope of the volume. Chapter X. contains a thorough account of the theoretical aspect of the Phase Rule, and gives a number of well-chosen illustrative examples of the use of this law. Chapter XII. deals with

Chemical Affinity; Chapter XIII. is devoted to the Nernst Heat Theorem and its bearing on chemical phenomena. The first part of Chapter XIV. describes the theory of Light Radiation, and the second and larger part is a systematic account of Photochemistry.

As the author states in the Preface to Volume I., first edition, the book is not intended for beginners. With the volume at present under review, a working knowledge of the facts and elementary theory of physical chemistry is assumed. The student need not, however, possess any previous knowledge of thermodynamics, as the first four chapters are chiefly devoted to a treatment of thermodynamics in general. The exhaustive manner in which the thermodynamical theorems used are deduced from first principles makes these chapters extremely valuable, not to the chemist only, but also to the student of pure physics.

It is rare that a rigorous and methodical system of treatment of a science is found together with lucidity and ease of style. That Professor Lewis has succeeded in this difficult task may be seen in the popularity of the first two editions of his work, which may, indeed, be said to be indispensable to all students taking an Honours Degree in chemistry, or pursuing the study of physical chemistry.

H. R. AMBLER.

OPTICAL METHODS IN CONTROL AND RESEARCH LABORATORIES. London: Adam Hilger, Ltd. Pp. 30. Price 1s. 6d. net.

This little work draws attention in concise language to the applications of optical determinations to applied chemistry; it is divided into four sections, dealing with the spectrometer and spectrograph for emission spectra, absorption spectra and spectrophotometry, the refractometer, and the polarimeter respectively. That an optical determination is rapid, that it involves the loss of very minute quantities of a sample, and that the information deduced from it is often of much value, are commonplaces, and there are few analytical laboratories without a spectroscope, a refractometer, and a polarimeter; it is safe, however, to say that even the most persistent devotee of optical methods will find much that is suggestive and new.

It is marvellous what a wide range is touched upon in so small a book; references to a long list of papers giving the details of working methods are very numerous. The one omission is the failure to emphasise the importance of the information to be obtained by combining an optical with another physical determination; thus refractive index plus density will give control figures for both extract and alcohol in many substances, will estimate malt solids and cod-liver oil in malt and oil preparations; refractive index and rotatory power will enable the crystallisation of alkaloid solutions to be followed, and the combined determinations often yield results unobtainable by either method alone.

The fact that the book is published by a leading firm of optical instrument makers suggests that it is an advertising brochure, but its useful suggestiveness is so great that it is a form of advertisement to be encouraged.

H. DROOP-RICHMOND.

LABORATORY MANUAL OF ORGANIC CHEMISTRY. By H. L. FISHER. London Chapman and Hall. 1920. Price 19s. 6d. net.

This book should prove a useful guide to the study of practical organic chemistry; the material is well arranged and presented in a manner calculated to maintain the interest of the student.

Amongst the more notable features is the account of experiments dealing with the conversion of pinene to camphor, in which the student actually carries out a synthesis involving a fairly lengthy series of operations. It is sometimes difficult to get the youthful chemist to realise the importance of obtaining his products, not only in a state of purity but also in good yield, and the performing of a synthesis, involving a number of separate reactions, is perhaps one of the best means of emphasising the importance of the second desideratum.

The completeness and excellence of the section on the determination of carbon, hydrogen, and nitrogen gives one a feeling of regret that the author does not include an account of methods for the estimation of halogens, sulphur, and phosphorus and also of the commoner organic radicals.

The questions at the end of the various sections of the book are generally well chosen, and should go far towards arousing an intelligent interest in the subject, and so tend to eliminate what might be called "cookery book" chemistry.

The volume is well produced; the clearness and excellence of the diagrams leave little to be desired, and the typographical errors are relatively few in number. Attention may be called, however, to an obvious error of punctuation on p. 264, and to the use of the word "practice" on p. 117 where the verb is intended, although possibly this may be intentional. The following minor points may also be noted: The misspelling of bromnaphthalene on p. 17; the density of aniline is quoted on p. 161 at $\frac{1}{4}^{\circ}$ —presumably meaning the density of aniline at 16° compared with that of water at 4° —the more usual nomenclature $\frac{1}{4}^{\circ}$ seems to be preferable; on pp. 178 and 204 the boiling-points ascribed to phenol do not agree—this is the more regrettable as the author lays much stress on the "correction" of thermometric data.

In the preparation of a tertiary alcohol by means of Grignard's reaction (p. 70) it is surely not necessary to have so large an excess of ethyl bromide as that given in the directions—namely, 100 per cent. In the experience of the reviewer a 10 to 20 per cent. excess of ethyl bromide is usually quite sufficient to bring about complete solution of the magnesium.

There are several innovations in terminology—namely, the use of 1° , 2° , 3° for primary, secondary, and tertiary, and of the word "nitronation" for the process of nitration as distinct from the formation of nitric esters. The wisdom of the first appears to be questionable, and any gain of accuracy from the use of the second would probably be outweighed by the confusion it would cause.

JOSEPH KENYON.

RECENT ADVANCES IN ORGANIC CHEMISTRY. By ALFRED W. STEWART, D.Sc. Fourth Edition. London: Longmans, Green and Co. 1920. Price 21s. net.

The appearance of a fourth edition of this well-known book so soon after that of the third is in itself a clear indication of the value and interest of the work. The present volume does not differ greatly from its predecessors in general character; hence it is unnecessary here to outline its scope. New matter has been added to bring each section thoroughly up to date, so that those who wish to keep themselves abreast of the times may have every confidence that no really important work, dealing with the theoretical side of organic chemistry, has been overlooked. It is obviously impossible in some 350 pages to go deeply into detail; but there are abundant references to original papers of dates extending to 1920.

Of the new material incorporated in the present edition, special attention may be called to the fresh section added to the chapter on the polypeptides. Here is traced the connection between these synthetic substances and the naturally occurring proteins. The lines along which the compositions of the latter are being approached are clearly indicated, but little hope is given that this most complex problem will be solved in the immediate future. One of the most interesting and important additions in the present volume is the last chapter, entitled "Some Unsolved Problems." Why is carbon unique in its capacity for chain and ring formations? Why should the *number* of carbon atoms in a ring have so great an influence? What are the principles underlying "Crum Brown's Rule"? Why are some compounds stable, while others of similar structure are either unstable or even non-existent? What is the mechanism of intramolecular change? These are a few of the problems presented to the reader as awaiting solution. In some cases indications are given of possible solutions; in others we must look to future years to provide the key. None the less the statement of these difficulties is of great value. In the first place it reminds us of the limitations of our present knowledge: how we are still very much on the outer surface of things, as it were, and really know little of internal structure and of the forces at work in holding atoms in combination. Useful, nay indispensable, as our ordinary plane formulæ are, we need to be reminded that they can hardly portray the actual arrangement of atoms in molecules; yet three-dimension formulæ have at present little application apart from the phenomenon of stereoisomerism. Recent research has thrown much light on the structure of crystals and of atoms; is it too much to hope that in the near future some new method of investigation will reveal to us the secrets of molecular structure? Secondly, to be confronted with an array of problems awaiting solution is not only a stimulus to further research, but also an indication of the topics on which fresh knowledge is specially required. As the author points out in his preface, too much time is spent, one feels inclined to say wasted, on the preparation of numberless new compounds of scant interest in themselves, which, at present at any rate, have no practical application, and also are unlikely to add anything to our understanding of the essential nature of chemical combination. This book provides a clear exposition of the methods by which, in the last few years, the compositions of many complex

substances have been unravelled ; it cannot fail to be of great assistance to those who will be called upon to handle the still more complex problems of the future.

The two indexes are fully adequate to their purpose. A. F. KITCHING.

NUCLEIC ACIDS: THEIR CHEMICAL PROPERTIES AND PHYSIOLOGICAL CONDUCT. By WALTER JONES, Ph.D., Professor of Physiological Chemistry in the Johns Hopkins Medical School. London. Second Edition. New York: Longmans, Green and Co. 1920. Price 9s. net.

Progress in all fields of biochemical research is so rapid that it is difficult for the literature to keep pace with it. Having regard to the very great importance and to the great complexity of the problems with which biochemists are concerned, it is perhaps more necessary than in any other branch of chemical science that the investigator and the student alike should have the opportunity from time to time of obtaining, by reference to authoritative and reliable monographs, a clear survey of the existing state of knowledge. It is for this reason especially that we welcome the second edition of Dr. Jones' monograph, the first edition of which appeared in 1914. Since that date considerable additions have been made to our knowledge of the nucleic acids and their physiological behaviour, and these are all fully and clearly dealt with in the present volume.

A detailed review of this work in a journal devoted to analytical chemistry would clearly be out of place. As showing, however, how important a bearing biochemical investigations may have upon purely biological questions, the reviewer cannot refrain from referring to the very interesting and recently established fact that in respect of purine metabolism, the higher apes resemble man in that they are unable to convert uric acid into allantoine, whilst in the lower mammals, including the monkeys, this change is readily effected.

To many analytical chemists, and especially to those who have to deal with problems of food chemistry, some knowledge of the chemistry and physiological behaviour of the breaking-down products of the nucleo-proteins is necessary, and no safer and clearer guide than the work under review could be recommended or, indeed, could be desired.

In a very comprehensive Appendix will be found collected the more important analytical reactions of the purine and pyrimidine derivatives, as well as of the nucleosides and nucleotides—information which, as far as the writer knows, is not available in a collected form in any other publication.

The book is written not merely in a lucid, but in a very attractive manner, and by one who can claim to speak on the subject with authority. It is remarkably free from typographical and other mistakes, and is well printed.

The reference on page 15 (in connection with the structural formula of uric acid) to Medicus having "made a place for himself in history by his ability to guess the correct formula" is not very generous, even though it contains a grain of truth. In his Paper, published in 1875, dealing with the constitution of uric acid and of some of its derivatives, Medicus based his conclusions on a consideration of

the experimental results obtained by Strecker and others, and arrived at the formula which was subsequently proved by Emil Fischer and by Behrend and Roosen to be the correct one. It may be mentioned, incidentally, that it was this same work of Strecker which led directly, in the hands of Horbaczewski, to the synthesis of uric acid.

This book is deserving of unqualified commendation, and constitutes a very valuable addition to the excellent series of monographs on biochemistry, for the editing of which Dr. Plimmer and Dr. Gowland Hopkins are jointly responsible.

A. CHASTON CHAPMAN.

AN INTRODUCTION TO THE CHEMISTRY OF PLANT PRODUCTS. By PAUL HAAS, D.Sc., and T. G. HILL, A.R.C.S. Vol. I. Third Edition. London: Longmans, Green and Co. 1921. Price 16s. net.

The fact that in bringing out the third edition of this book the authors have found it necessary to enlarge it so as to occupy two volumes is sufficient proof of its popularity. The present Vol. I. contains most that was in its predecessors, some improvements having been introduced in the arrangement and order of the subject-matter. The section devoted to colloid chemistry is practically new and now presents a clear and interesting summary of the present position of that subject. The second volume, which is in preparation, is to be devoted more exclusively to plant physiology.

The authors have, for the purpose of compiling this manual, laid a very large field of literature under contribution, and as a compendium of chemical information of use to botanists we do not think that it has a rival in this language. If the book has a fault, it is that the student is given too little guidance in selecting the fundamental and important from among a mass of facts and conflicting opinions. For example, the section on starch (p. 114 *et seq.*) forms an instance where clearness has been sacrificed to multiplicity of detail.

The practical part of the book consists of a number of qualitative experiments grouped at the end of each section, illustrating some of the reactions of the substances previously dealt with theoretically, together with a selection of quantitative estimations of the same substances. It is in the latter that we think that the authors have missed an opportunity for affording help to the botanist with biochemical leanings. In the section on "fats," for example, the routine methods for fat analysis employed in commercial laboratories—saponification, acid, acetyl, and iodine values, etc.—are described, but no attempt is made to show how these may be applied to tracing the changes which take place in the fat of plant tissues during various stages of growth.

The interpretation of the insoluble bromide test (Hehner and Mitchell) is misleading; the weight of the precipitate obtained is *not* proportional to the amount of unsaturated fatty acids present, but is merely an indication of the amount of triglycerides containing acids of the linolenic series. The method selected for the preparation of lecithin by means of the cadmium chloride compound might usefully have been exchanged for the more recent acetone-precipitation method.

The section on carbohydrates gives a useful account of the most important members of the group, though a mistake in describing xylose as optically inactive has crept in. The section on the estimation of sugars fails to appreciate the difficulties of the botanist in the preliminary treatment of tissue. Examples of the estimation of mixtures of sugars are given, but the *combined* use of the polarimeter and the reduction method is not described. The estimation of maltose is made needlessly confusing, and the hydrolysis of this substance is termed "inversion." It is difficult to understand why the reduction methods of Fehling and Pavy are described when they have been superseded by many others equally simple and more reliable, such for example as that of Bertrand.

The chapter on plant pigments is a clear account based largely on the work of Willstätter and his pupils, and includes some discussion on the physiological aspect of the subject. It is surprising to find that the authors have included (p. 256) a method for the preparation of phycoerithrin from red sea-weed, consisting in the precipitation of the aqueous extract of the tissue with methylated spirit, by which means the pigment (together with protein and other impurities) is thrown down. "The pigment in a pasty mass . . . is dried in a vacuum," after which it is found to give most of the protein reactions. "From these and other facts it is concluded that phycoerythrin is a colloidal nitrogenous substance allied to the proteins." It is from methods and conclusions such as this that a knowledge of biochemistry should protect the botanist.

The chapter on enzymes is a clear treatment of the broad theoretical aspects of the subject, besides giving much detailed information of use to botanists. It is a little misleading to head a paragraph "The Isolation of Zymase" when the preparation of an aqueous extract of yeast containing the enzyme is intended.

M. STEPHENSON.

THE YEASTS. By ALEXANDRE GUILLIERMOND; translated and thoroughly revised in collaboration with the original author by FRED WILBUR TANNER. Pp. 409. New York: John Wiley and Sons. 1920. Price 33s. net.

This English edition is based on Guilliermond's "Les Levures," which was published in 1912, and to which numerous additions and modifications have now been made by both author and translator.

The language of the book is often slipshod and sometimes not readily intelligible, and orthographic and other errors, more especially in the names of authors, are to be numbered by the dozen. The following few examples must suffice: "Separated closely from" (p. 7); "The cells bud generally at their extremities; this is exceptional only when lateral budding is proven" (p. 10); "S. Ludwiggii did not keep longer than 2 years, often 6, . . ." (p. 165); "concurrence" is used to denote "competition" (p. 154); "microscopic" appears for "macroscopic" (p. 167); "Sur l'habitat et la conversation des levures spontanées" (p. 256). Schützemberger, DuClaux, Linder, Boyen-Jensen, Noegeli, Pearse, and Van Tieghm all occur, some of them repeatedly, while Haydruck is given for Hayduck throughout.

Luckily chemistry and physics do not figure to any considerable extent in the

book, for in these subjects the author—or is it the translator?—rapidly gets out of his depth. Thus we find: “They [certain yeasts] act on the melibiose which they change to dextrose and galactose; this is fermented to *d*-glucose” (p. 63); “hydrocarbon” is used twice on p. 54 and again on p. 161 with the meaning of “carbohydrate,” whilst on p. 75, “hydrocarbon compounds” serves as a heading for substances able to supply the requirements of yeasts as regards carbon compounds; the “thermal deathpoint” is defined as “the amount of heat which is necessary to destroy the yeast” (p. 168).

In spite of these and many similar blemishes, the book well deserves perusal by all interested in yeasts, whether from a scientific or from an industrial point of view, and it is to be deplored that the publishers have found it necessary to demand such a high price. The treatment of the subject is predominantly botanical and in this direction may be regarded as reasonably complete, although one or two striking omissions force themselves on the notice of the reader. Noteworthy among these is the absence from the section dealing with the characteristics of alcoholic fermentation, and also from the excellent bibliographical index, of any reference to Adrian Brown's work on the influence of oxygen and concentration on alcoholic fermentation, on the specific character of the fermentative functions of yeast cells, etc.

The subjects dealt with in the various chapters are: Morphology and development of the yeasts; cytology of yeast; physiology, nutrition, respiration, and alcoholic fermentation; origin of the yeasts, their position in classifications of the fungi and their systematic relationships; methods of culture and isolation of yeasts; methods for characterising and identifying yeasts; variation of species; classification of the yeasts; family of saccharomycetes; family of non-saccharomycetes or doubtful yeasts; pathogenic yeasts; fungi related to the yeasts. In general the facts are presented fairly and lucidly, and objection can scarcely be taken to the prominence given, here and there, to the author's own views and results. Especially valuable are the last four chapters, which contain descriptions of about 300 yeasts and allied micro-organisms, and occupy nearly 200 out of the 380 pages of the text of the book; this section is well illustrated.

The bibliographical index extends to nearly 30 pages, and is followed by name and subject indexes. The printing and general style of the book are of the high standard of excellence usually associated with Messrs. John Wiley's productions.

T. H. POPE.

BIBLIOTHECA CHEMICO-MATHEMATICA. By H. ZEITLINGER and H. C. SOTHERAN.
Vols. I. and II. Pp. 964, including Index. London: H. Sotheran and Co.
Price 63s. net.

One of the authors points out in his preface that this is “perhaps the first historical catalogue of science published in any country, at least as giving at once the current price of each book included, bibliographical particulars, and many historical references, both in the descriptions themselves and in the notes.” Although the price of each book is quoted, it must not be assumed that this work is merely a

booksellers' catalogue, as it really contains a great deal of useful and interesting information which is not readily accessible elsewhere.

One is, perhaps, tempted to enquire why this work includes some comparatively modern books, and was not restricted to those published before a certain date; presumably this was impossible in what is in part a price-list, but the effect is curious, and it is surprising to find such works as Newton's "Principia" of 1686 rubbing shoulders with the second edition of Lewkowitsch's "Oils and Fats of 1898." Unfortunately the catalogue is not complete, and while a good many of the earlier books dealing with analysis are included no reference is made, for example, to Winter Blyth's "Foods," though more recent and less important works are mentioned. In spite of its incompleteness, this catalogue cannot fail to be of permanent value as a book of reference, particularly to those who are interested in the fascinating study of the history of chemical science.

A rather striking point is the low market value of many of the older and rarer books, even such a landmark in the progress of science as a first edition of Newton's "Principia," which is quoted as "excessively rare," may be had for a modest eighteen guineas. When one considers the high prices often paid for first editions of "belles lettres," one feels that there must be a lack of appreciation of historical science, or that those interested in it are too few or too impecunious to cause the price of old and rare scientific books to rise to a high level.

The catalogue is very well arranged and indexed, and contains numerous reproductions from photographs of interesting plates. The authors are to be congratulated on the result of their painstaking and laborious task.

R. G. PELLY.



THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

THE FORTY-THIRD ANNUAL GENERAL MEETING OF THE INSTITUTE OF CHEMISTRY was held on March 1 at the Institute's house in Russell Square. Sir Herbert Jackson, the retiring President, in the course of his address, remarked that Government departments and official authorities generally had shown more inclination in recent times than in the past to accord higher recognition to the services of men of science. The conditions of appointments of chemists, both in the Government service and in industry, had been improved, and until the close of 1920 the profession had been in almost a unique position in that very few indeed of its members were disengaged. The prevailing depression in industry had had some effect on the employment of chemists, but even now less than fifty were disengaged out of nearly 3,300 on the Roll. The By-laws of the Institute had undergone revision to provide for the representation of chemists from various parts of the country and practising in different departments of work, and alterations have been made to define more specifically certain points relating to the ethics of the profession and further to restrict the membership of the Institute to British subjects. The Institute was taking part in many matters affecting the public life of the country where chemistry was concerned, and the Annual Report showed that chartered professional bodies of this character were able to render the State valuable service. The greater consideration given to science by the Government was an encouragement to the coming generation of chemists to follow a career of essential and vital importance to the needs of the country. It would probably be regarded as desirable at the present moment for the Council of the Institute, without taking part in politics, to give expression to their views on the grave importance of maintaining in this country industries on which not only the future development of our chemical industry and many allied industries depends, but the future of a very large number of students of chemistry who are now in the course of training. The Institute was entrusted by its Charter with securing the supply of well-trained chemists, but, unless a great chemical industry were maintained, there would be a very poor prospect for them. The President maintained that the Institute had throughout its existence fulfilled the purposes for which it was incorporated. It had kept alive the corporate spirit of the profession, the means whereby the opinions and views of its members found expression in matters of public concern. It was the officially recognised public body to whom the country could turn for advice and guidance on matters relating to the profession. It rendered every possible assistance to those who intended to follow the profession of chemistry, and promoted and maintained the highest standard of training and competence for that profession. It registered the trained and competent, and thereby supplied competent professional service for the country. Moreover, it promoted the strictest integrity on the part of its members in their dealings with one another and with the public, and fostered by every means in its power the status of the profession. He was confident that it would continue to gain strength and prestige.

The adoption of the Report and a vote of thanks to the President for his address were moved by Sir William Tilden and unanimously carried.

The Officers and Council were elected as nominated, and the Censors and Auditors were elected for the ensuing year. Mr. Alfred Chaston Chapman, F.R.S., succeeds Sir Herbert Jackson as President.



SCIENTIFIC AND INDUSTRIAL RESEARCH DEPARTMENT.

THE Secretary announces that the following Associations have been approved by the Department as complying with the conditions laid down in the Government scheme for the encouragement of industrial research :

The British Research Association for Liquid Fuels. *Secretary*, Percy Still, M.I.E.E.,
19, Cadogan Gardens, S.W. 1.

The Research Association for Cast Iron and Allied Industries. *Secretary*, T. Vickers,
174, Corporation Street, Birmingham.

The Secretary also announces that the Lord President of the Council has established an Inter-Departmental Committee on Patents, with the following terms of reference: (1) To consider the methods of dealing with inventions made by workers aided or maintained from public funds, whether such workers be engaged (a) as research workers, or (b) in some other technical capacity, so as to give a fair reward to the inventor and thus encourage further effort, to secure the utilisation in industry of suitable inventions, and to protect the national interest; and (2) to outline a course of procedure in respect of inventions arising out of State aided or supported work, which shall further these aims and be suitable for adoption by all Government Departments concerned.

The Secretary to the Committee is Mr. A. Abbott, to whom all communications should be addressed at 16 and 18, Old Queen Street, Westminster, London, S.W. 1.

**THE FINE CHEMICALS INDUSTRY.**

THE leading British makers of fine chemicals have published a letter in which they point out that this industry is of national importance, and desire to submit to public knowledge the following facts: (1) The application of chemical science to industry is essential to the preservation of our world position in commerce; (2) essential plant erected during the war years could be adapted to peace purposes, but must become idle and useless unless the State take measures for its safeguarding; (3) the fine chemical industry provided during the war, *inter alia*—(a) essential medicinal preparations; (b) higher forms of explosives and gases; (c) photographic chemicals, and (d) research chemicals; (4) British science and chemical manufactures are in no respect inferior to the science and manufactures of competing nations.