OCTOBER, 1939 Vol. 64, No. 763

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

Food Inspection and Analysis in Holland

By J. STRAUB, Chem.Ing.

(*Director of the Food Inspection Laboratory, Amsterdam*)

(*Read at the Meeting, April* 5, 1939)

As a member of your Society, it affords me great pleasure to give some account of my daily work in connection with food inspection and analysis. Some of you may have been present when a party of English food chemists paid a visit to my laboratory in 1936.

Food chemistry is a branch of applied science. That is to say, it is studied not for its own sake—simply for the pleasure of knowing so much more of Nature's secrets—but for the material benefit to mankind that is to arise from it. Scientific methods are used to solve chemical problems that have social results as an ultimate aim.

Research work in Holland offers several good examples of the fundamental rôle that analytical chemistry has played in advancing our knowledge of all branches of food chemistry. Thus, in the first place, I may mention the recent work of Jansen,[1] Professor of Physiological Chemistry in Amsterdam, who (with his pupils, Cohen, Wiegand and others) worked out a simple chemical method for the quantitative estimation of vitamin B_1 in food and in urine. This opened the way to the exact study of vitamin B_1 metabolism, and for work on the diagnosis, cure and prevention of B_1-avitaminosis. The vitamin is adsorbed on acid clay (frankonite) and oxidised to thiochrome, and the fluorescence of this substance in ultra-violet light is measured with the fluorometer of F. H. Cohen.*

At Utrecht University, Prof. Wolff and pupils have done much work on vitamins A and C. Existing methods of estimating these substances have been studied, simple chemical and micro-chemical methods for routine work have been

* Obtainable from Adam Hilger, Ltd.

worked out for vitamin A, for carotene and for vitamin C, and these methods have been applied to fruits and vegetables, milk and animal products, so that complete lists of the vitamin-contents of various foods could be compiled. This list proved to be of great value as a basis for a critical survey of the diet of certain groups of the population, especially the poorer classes and the unemployed, in Holland. The application of the methods to urine and blood affords the possibility of recognising malnutrition or incipient vitamin deficiency. A complete set of papers on the chemical estimation of vitamins has been published in the report of a meeting, held in 1938, of all Dutch workers in this field.[2]

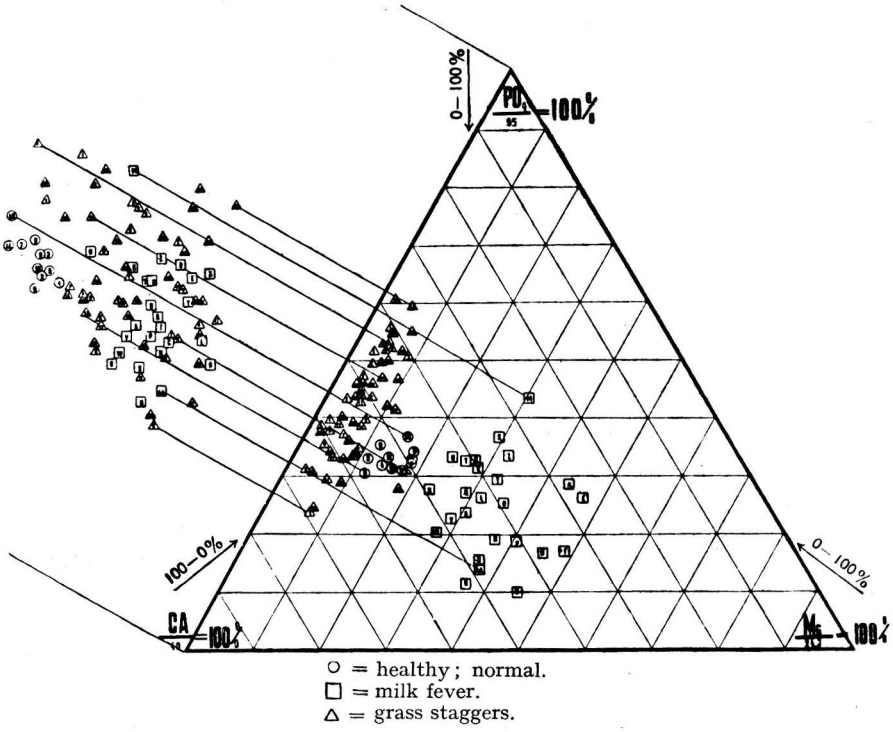


FIG. 1

Relative concentrations of Mg, Ca and PO_4 ions in blood serum of normal and diseased cows. The spots outside the triangle give the absolute values for Mg + Ca + PO_4 (B. Sjollema, 1929. Ref. 5).

Reference may be made also to the work of the Department of Veterinary Chemistry of Utrecht University, where the analysis of food, especially of cattle-food, has led to far-reaching results. Here Prof. Dr. B. Sjollema, Dr. L. Seekles and their co-workers found that various diseases of cows were specifically caused by deficiency of certain metals in the diet. Cows are particularly sensitive to small deviations in the mineral-content of the feed, because every day they excrete in their milk much mineral matter and many different elements, and so run the risk that their bodies may be entirely deprived of some indispensable constituent.

Various published methods for estimating traces of copper in grass and in the soil of meadows, in cattle-food, in milk and in blood were tested[3] and adapted to

the material in hand (carbamate method, thiocyanate method). The copper-content of different samples showed wide variations. The endemic cow disease "pine" and also a newly observed disease with other symptoms were proved to result from copper deficiency. Sjollema[4] cured them by spraying a small quantity of copper sulphate on the meadow or by giving it to the cows.

Much work has also been done on the calcium, magnesium and phosphate contents of feeding stuffs and blood. Here, again, Sjollema[5] and Seekles discovered the cause and the remedy for two diseases. "Grass staggers" proved to be associated with magnesium deficiency, and milk-fever with relative magnesium excess. The results for the three constituents were plotted in triangular graphs, so that differences in the relation of the different ions could be easily seen (Fig. 1).

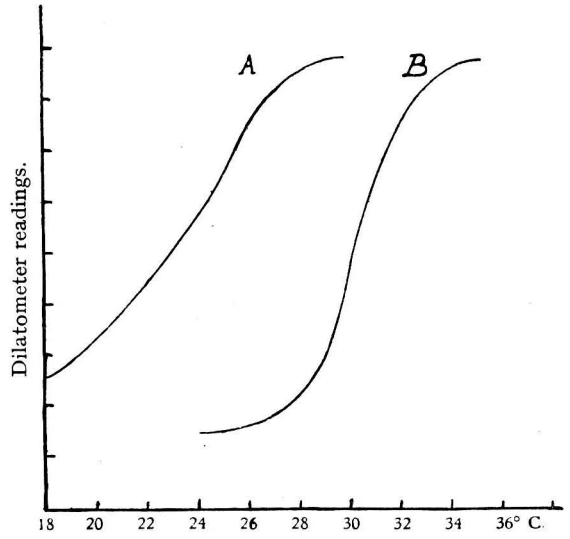


FIG. 2

Dilatation of cocoa butter with rising temperature, showing the effect of gradual melting. B is a curve for cocoa butter, recrystallised by keeping it in the dilatometer for 15 hours at 24° C. (J. D. van Roon, 1930. Ref. 14).

Apart from this University work, food research is carried out under the Department of Agriculture. I might remind you of the latest achievement of my friend Kruisheer,[6] who with his staff worked out a mechanical device for measuring the consistence of butter. The hardness or softness of butter is a somewhat important property in trade, although it has nothing to do with the taste and the nutrient value. Housewives are particular about it, as they have to spread the butter, and so the consistence has become one of the elements in grading butter for the grocery trade. Hence it is useful to have available an objective measuring instrument, which can also be of great service in investigations to improve the consistence of butter. Kruisheer's ingenious instrument gives an exact reading of the force used in pushing with a constant velocity a metal cylinder into the butter.

Kruisheer's former work on food analysis was done at the time he was a Public Analyst. His method[7] for estimating honey in honey-cake is generally accepted and gives accurate results. It is based on the fructose method first described by Kolthoff[8] (oxidation of aldose with excess of iodine and caustic soda, followed by quantitative copper reduction, preferably by Schoorl's method)[9]. His method for estimating hydroxymethylfurfural in wines, which has also met with general acceptance, has proved of great help in distinguishing genuine wines from products that have been sweetened with invert sugar or concentrated grape-juice. From this work he went on to devise methods for the estimation of laevulosin and inulin, which are useful in the analysis of coffee extract for chicory and caramel.[11]

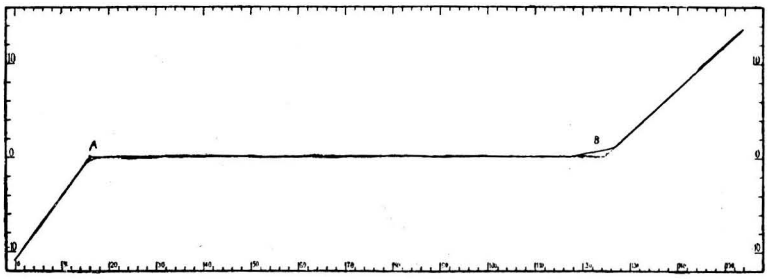


FIG. 3

Fusion line for 2·9 g. of ice, as used to check the calorimeter constants (Straub and Malotaux, 1933. Ref. 17).

Of late years food industry in Holland has occupied the attention of many chemists. Very little of their work, however, is published, although some good analytical studies have been made.

Ch. Doppler,[12] of the well-known Droste cacao mills, published analytical studies on cell-wall substances of the cacao bean.

Bertram,[13] formerly of van den Berghs, Ltd., published his now well-known permanganate method for estimating saturated and unsaturated fatty acids in fats, and the A and B number method for estimating butter-fat and coconut oil in margarine. He is also reputed to be the first inventor of a method of determining the solid-liquid partition in fats at different temperatures by means of the dilatometer. The method was devised independently and published by van Roon,[14] at that time chemist to van Houten's cocoa works (Fig. 2).

Other analytical work of importance to the fat industry has been done in the laboratories of Delft Technical High School and Rotterdam Trade University. Steger and van Loon[15] (Delft) published detailed modern analyses of various vegetable oils, including the determination of the content of oleic acid isomers, elaeo-stearic acids and couepic acid (= licanic acid). In Verkade and Coops's work[16] (Rotterdam) a method for analysing the very complex mixture of fatty acids of natural fats by fractional distillation of methyl esters and by physical analysis (melting-curve) of the binary mixtures that distil has been devised.

In this connection something may be said about the work of Malotaux[17] and myself on fats. We recognised long ago that the change of consistence with temperature was an important factor in the palatability of edible fats. Whilst

van Roon used a dilatometric method to obtain numbers and graphs for this property in different fats, we made use of a calorimetric method. Both depend on the idea that one of the major elements in consistence is the proportion of solid to liquid glycerides in the fat. With rising temperature solid parts gradually melt, that is to say, they are dissolved in the liquid part. This change is accompanied by a change in volume and so can be followed by means of the dilatometer.

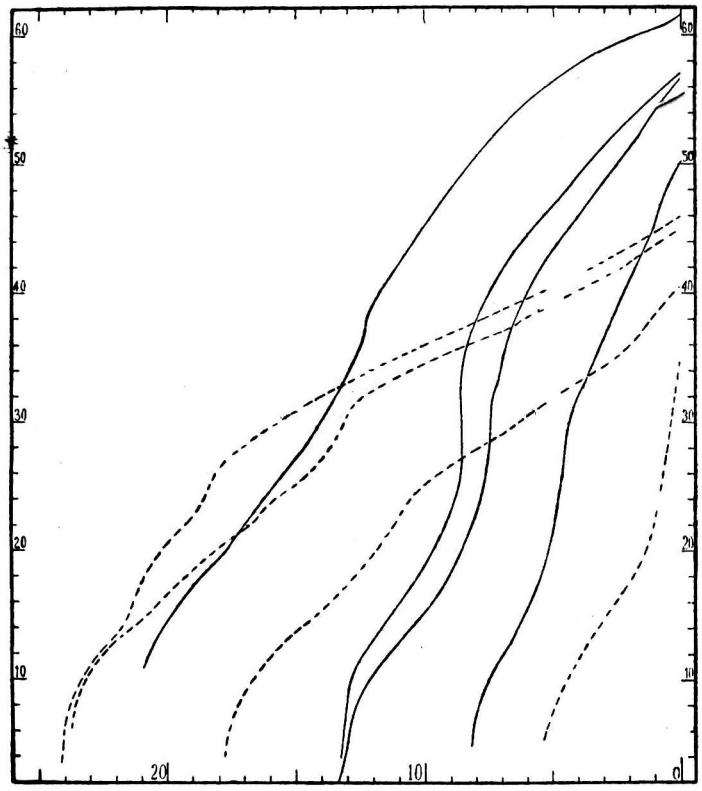


FIG. 4

Gradual change of consistence curve for sesame oil during hardening with nickel and hydrogen. The dotted lines and continuous lines represent two different hardening processes (Straub and Malotaux, 1933. Ref. 17).

It is also accompanied by an absorption of the heat of fusion and so can be followed calorimetrically. Although the apparatus is simple in principle, it must be very carefully made. The fat to be melted is put into a silver crucible; for better transmission of heat this cylindrical thimble contains a fine network of metal gauze. A thermometer is placed in the centre and the whole is fixed in a glass bulb; this is put in a water-bath together with a thermometer, and the test is started. The bath is heated in such a way that there is continually a difference of 10° C. between the two thermometers, and exact readings are taken every minute, a stop-watch being used.

After an hour the fat is fully melted and the readings are plotted as a graph. There is a horizontal time-axis and a vertical temperature-axis. Fig. 3 illustrates

an experiment in which there is pure water in the thimble. Starting from −10° C., we have first the warming of the ice from −10° to 0° C., then at 0° C. complete melting, and lastly the warming of the water.

With the constant difference of temperature there is a constant transmission of calories, so that 1 minute means exactly 2 calories, 40 minutes indicate 80 calories, and 80 calories correspond with one gram of water melted. Thus the calorie scale is used as a quantitative scale for the solid-liquid transition. When the method is applied to fat it is advantageous to correct the curve, by subtracting from readings the known amount of heat necessary for warming the sample, and so to take into consideration only the unknown amount of heat used for melting.

An example will give some idea of the very specific results that the method

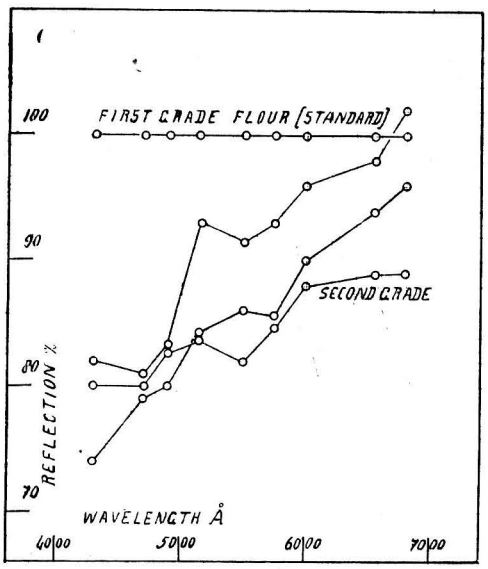


FIG. 5

Percentage reflection of light of nine different wave-lengths by first grade and second grade bakers' wheat flour (bleached) and by two intermediate samples. Differences amplified by the method of Straub and Simons. Filters and comparator of A. Hilger, Ltd.

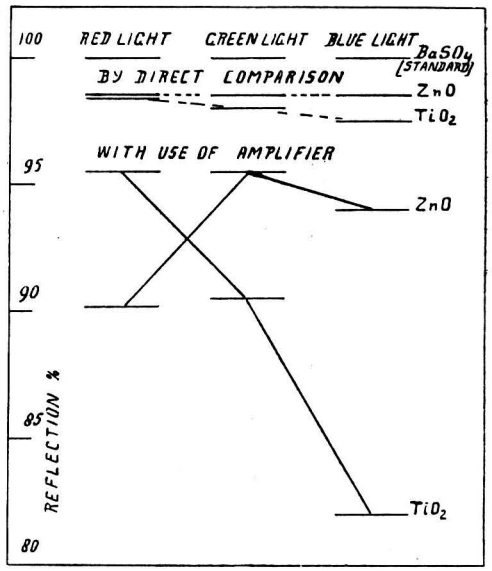


FIG. 6

Percentage reflection of red, green and blue light by ZnO and TiO_2 powders, measured by comparison with standard $BaSO_4$ powder (*a*) by direct comparison of flat surfaces, (*b*) with the use of Straub and Simons' amplifier.

gives. In the process of hardening fats, solid material is gradually formed. Samples of soya-bean oil, taken from the hardening drum every 15 minutes, were examined calorimetrically and showed lines grouped like the spokes of a fan (Fig. 4). Then a second method of hardening (at a different temperature and pressure) was followed, and quite another set of curves was obtained; this demonstrated that in the second method more solid (and with a lower melting-point) was formed, so that a much better product for edible purposes was obtained (see Fig. 4, dotted lines).

There is yet another method used in my laboratory about which I should like to say a few words, the more so as I have found English instrument makers,

Messrs. Adam Hilger, Ltd., willing to make the instrument required. This is a method for measuring the whiteness of such substances as wheat flour, paints or paper. I will begin by giving some experimental results in the form of graphs (Figs. 5 and 6). Good wheat flours of low, but somewhat varied, milling grade, and with ash-contents ranging from 0·3 to 0·6 per cent., show slight differences in whiteness, which can be seen by experts, but can hardly be measured colorimetrically except by very sensitive photo-electric cell methods. In simple subjective colorimetry the difference amounts to only about 2 per cent. with light of any colour. There is about the same degree of difference between white paints. With the simple instrument devised in collaboration with my friend, Mr. Simons, we amplify colour differences about tenfold, so that subjective colorimetry ten times as sensitive as the discerning power of the eye becomes possible. Readings are made from blue to red in the spectrum with a number of different light-filters. A heavily bleached flour of the very first grade and with low ash-content is used as a standard. The principle of the amplification is to bore a hole of well-defined dimensions in the flour samples and to measure the light reflected from the bottom of this hole.

The instrument, for which a patent application has been made, consists of two tubes for the flour samples, fixed in the bottom of a metal bulb painted white inside. A powerful electric lamp in the bulb supplies good indirect illumination. The whole is just an accessory to a colour comparator and may be called a colour "amplifier," as suggested by Messrs. Hilger (the instrument as made by them will have two lamps in the bulb). It is obvious that here, again, an analytical method gives a basis for research. In the quest for whiter material an exact means of measuring whiteness must first be found.

So much about methods of general interest used in my laboratory. Of course many special methods must of necessity be devised in the laboratories of Public Analysts. I might mention here some work of my predecessor, van Raalte, the simple xylol number method[18] for estimating the butter-content of margarine and the method of recognising refined lard by its fluorescence.[19] Regulations on the composition of foods are of no use if they cannot be maintained or enforced, and this cannot be done if there is no satisfactory method of analysis available to ensure that commercial products are up to standard. For example, a regulation to the effect that milk bread must be made with milk was issued, when Public Analysts had worked out an exact method for determining butter-fat in presence of other fats and milk sugar in presence of other carbohydrates.

Official methods are exactly described in the regulations and must be followed in so far as they are sufficient. Should they fail to disclose some new form of adulteration the analyst is at liberty to make use of his personal experience and resources. Many special methods have thus been devised or adapted to circumstances by our Public Analysts and have subsequently been included in the regulations for different foods; many, of course, have also been taken from the literature without any change and are the same as those used all over the world, such as, for example, the Feder number for added water in sausage, and the freezing-point for added water in milk.

There are now food regulations for every group of foods, all formulated on

the same plan. First, they give the definitions of the various foodstuffs with which they deal, and prescribe the names under which these foods must be sold and labelled. Then they give the minimum analytical values permissible for each foodstuff, and lastly a precise description of the analytical methods to be used. Some of them also contain detailed requirements as to the dimensions and hygienic condition of shops and factories. As quite a new feature in this legislation I should mention that for some groups of packed foods the net contents must be stated on the package. The regulations promote general hygiene and protect the public from fraud and the trade from unfair competition. The intricate task of drawing them up is carried out by joint committees of government officials and leading manufacturers and tradesmen. Most of the regulations have now been in force for about ten years, and have become so accepted by the trade that only slight infringements occur, and these are mostly stopped by simple warnings. If necessary, legal action can be taken, jurisdiction being based upon the Food Act of 1919,[20] in which are laid down the principles on which the regulations are based. Other details and a summary of the chemical requirements for various foods have already been published in THE ANALYST by van Raalte and myself.[21] The Act also prescribes the organisation of control. The country is divided into 15 districts with a laboratory in each of them. From these centres inspectors pay systematic visits to control the hygienic condition of shops and factories in towns and villages, to inspect the soundness of foods in shops and markets, and to take samples of articles that cannot be judged on the spot. These inspectors must be keen and expert in their work. Especially difficult and responsible is the work of those who inspect game, poultry and fish, because their judgment cannot be supported by chemical evidence. This legal scheme of control seems to me to be analogous to what is aimed at under your new Food and Drugs Act. Therefore you may be interested to know how many officials have appeared to be necessary for food control in Holland. The Amsterdam district consists of the town itself and all neighbouring communities to a distance of 15 or 20 miles. The total number of inhabitants is one million. I have fifteen full-time inspectors for outdoor work, and of these, five are experts in milk, six in groceries and allied products, two in fish, one in bread, and one in game and poultry. The number of shops that one man can inspect thoroughly in a day is about 25; a market, of course, takes more time, whilst the stall of a street vendor takes less. The total number of visits in 1938 amounted to 64,000. The number of samples analysed in 1938 was 30,595, of which 24,387 were samples of milk and milk products. The numbers for 1937 are published in the February issue of THE ANALYST.[22] In addition to this staff of inspectors and analysts, there is a small clerical and general staff, including an instrument maker.

However, it is not easy to compute from the conditions in circumstances so different in Holland the number that would be required in England. Much depends on what articles are submitted to the control; thus, for example, drugs are not under our control in Holland, whilst, on the other hand, the Laboratory has recently been charged with the supervision of traders in gas masks, and the control of shops selling mattresses, bedding and bed covers, the filling material of which must now be declared on a label. As regards the number of laboratory

workers much depends on the requirements for various foods laid down in the regulations and on the methods of analysis involved. In general, a new regulation demands more work both from the inspectors and from the analytical staff than one that has been in force for some years. Most important is the distinction between articles that have a long period of life such as groceries, canned foods and jams, and articles of which new lots are distributed or manufactured every day or week, such as milk, bread, ice-cream, sausages, fruit and vegetables, fish, game and poultry. This distinction must always be borne in mind, and by far the most attention must be given to the ever-changing stocks of perishable commodities.

I have learned much from English analytical work and I should be glad if, in my account of food inspection and control in Holland, I may have been of some service to English analysts in return.

References

By the courtesy of my Dutch colleagues I have been able to offer the Society of Public Analysts and Other Analytical Chemists a nearly complete set of reprints of papers cited.

1 *a–f.* B. C. P. Jansen, *Rec. Trav. Chim. Pays-Bas*, 1936, **55**, 1046; J. A. Wiegand, Thesis, Amsterdam (in German) and *Archives Neerlandaises Physiologie*, 1938, **23**, 281, 312, 331 (in German); F. H. Cohen, *Rec. Trav. Chim. Pays-Bas*, 1935, **54**, 133.

2. *Zeitschrift für Vitaminforschung*, 1938, **7**, 226–296 (also sold separately). Papers by L. K. Wolff, B. C. P. Jansen, A. Emmerie, M. van Eekelen, E. H. Reerink and J. van Niekerk, and L. W. van Esveld.

3. C. D. Steussy, *Biochem. Z.*, 1938, **296**, 355.

4 *a–b.* B. Sjollema, *Id.*, 1933, **267**, 151; 1938, **295**, 372.

5 *a.* B. Sjollema and L. Seekles, *Tijdschrift voor Diergeneeskunde*, 1929, **56**, 18.
b. *Biochem. Z.*, 1931, **243**, 316.
c. *Chem. Weekblad*, 1933, **30**, 98.
d. *Acta veterinaria neelandica*, Vol. I, Part 2, pp. 1–128. "Stoffwechselstörungen des Rindes."

6 *a–b.* C. I. Kruisheer, *Chem. Weekblad*, 1938, **35**, 719. See also *J. Soc. Chem. Ind.*, 1939.

7 *a–b.* ——, *Z. Unters. Lebensm.*, 1929, **58**, 261, 282.

8. I. M. Kolthoff, *Id.*, 1923, **45**, 146.

9. N. Schoorl, *Id.*, 1929, **57**, 572.

10 *a–b–c.* C. I. Kruisheer, *Id.*, 1935, **69**, 570. *Cf. Id.*, 1937, **73**, 1; 1937, **74**, 477.

11 *a–b.* ——, *Id.*, 1932, **63**, 413; 1933, **65**, 275.

12 *a.* C. Doppler, Thesis, Delft, 1936, with English summary (*b*).

13 *a–c.* S. H. Bertram, *Z. Deutsche Oel-und Fett Industrie*, 1924, **44**, 447, 459; 1925, **45**, 733; and Wizoff's *"Einheitsmethoden,"* 1930, pp. 87, 97.

14. J. D. van Roon, *Chem. Weekblad.*, 1930, **27**, 498.

15 *a–o.* A. Steger and J. van Loon, *Rec. Trav. Chim. Pays-Bas*, 1930, **49**, 745; 1931, **50**, 32, 591, 638; 1933, **52**, 593; 1934, **53**, 24, 28, 41, 197; 1935, **54**, 149, 284, 502, 988; 1938, **57**, 25, 620 (on Po-Yoak oil); Abst., ANALYST, 1939, **64**, 703.

16. P. E. Verkade and J. Coops, *Biochem. Z.*, 1929, **206**, 468.

17 *a.* R. N. M. A. Malotaux and J. Straub, *Rec. Trav. Chim. Pays-Bas*, 1933, **52**, 275.
b. —— ——, *Id.*, 1934, **53**, 128.
c. —— ——, *Id.*, 1937, **56**, 263.
d. —— ——, *Id.*, 1938, **57**, 789.
e. *Chem. Weekblad.*, 1934, **31**, 455.
f. *Id.*, 1938, **35**, 741.
g. *Tillmann's Handbuch der Lebensmittel Chemie—IV. Fette und Oele*, pp. 20–24.

18. A. van Raalte, *Z. Unters. Lebensm.*, 1927, **53**, 236.

19. ——, *Id.*, 1928, **56**, 195.

20. The Act "Warenwet, 1919," and Regulations are published in one volume by Schuurman and Jordens.

21. A. van Raalte and J. Straub, ANALYST, 1932, **57**, 15.

22. J. Straub, ANALYST, 1939, **64**, 116.

FOOD INSPECTION LABORATORY
AMSTERDAM, HOLLAND

March, 1939

Manganese and Caffeine Contents of some Teas and Coffees

By D. R. K. COLEMAN, A.R.C.S., D.I.C., M.Sc., A.I.C., and F. C. GILBERT, A.R.C.S., D.I.C., M.Sc., A.I.C.

(Work done under the Society's Analytical Investigation Scheme)

It is well known that tea contains an unusually high proportion of manganese as compared with other plant products; this manganese depends upon a relatively high proportion in the soil suitable for tea planting. Coffee and maté also contain manganese, though in smaller proportions. Hence it seemed possible and worth investigating if the manganese might be a factor affecting the synthesis of caffeine by the plant. It could hardly influence the formation of tannin, since other tannin-yielding plants do not show much manganese. The fact that tea and, to a less extent, maté and coffee, have in common relatively high proportions of caffeine and manganese suggested the possibility of a connection between the two; this survey was carried out with a view to ascertaining if any relation existed between the two constituents. The determinations were made on 15 samples of black teas and 6 samples of raw coffee beans.

Tea.—*Manganese.*—For the determination of manganese in tea, the method was based on that used by Broek and Wolff[1] for milk. It consisted in the destruction of the organic matter by nitric and sulphuric acids and subsequent oxidation of the manganese to MnO_4' by means of potassium periodate, the resulting colour being measured in a Lovibond tintometer.

To approximately 1 g. of the finely-powdered sample, weighed into a 500-ml. Pyrex Kjeldahl flask and moistened with a little nitric acid (reagent quality), was added 20 ml. of sulphuric acid (reagent quality), the mixture was heated to boiling, and more nitric acid was added dropwise in the usual manner. The addition of the nitric acid was continued until all organic matter had been oxidised and a colourless solution obtained on evaporating the liquid until white fumes appeared. One g. of potassium persulphate was added, and the solution was diluted and then evaporated to fuming. The cold solution was diluted and transferred to a 250-ml. conical flask, the Kjeldahl flask being rinsed with successive portions of water, until the volume of the mixture was about 100 ml. The solution was boiled to expel sulphur dioxide and cooled somewhat, 0·1 g. of potassium periodate was added, and the mixture boiled for a few minutes and then kept hot for half-an-hour to develop fully the pink colour. The resulting solution was diluted to a known volume (usually 200 ml.), and the colour was measured, in a Lovibond tintometer, in 50 ml. (or, if necessary, in a smaller volume diluted to 50 ml.). It was found advisable to re-develop the colour in the diluted solution, by heating with a small quantity of potassium periodate before taking the reading in the tintometer.

A calibration curve was obtained by treating 5 ml. of a manganous sulphate solution (0·1 mg. of manganese per ml.), prepared from standard potassium permanganate solution by reduction with sulphur dioxide, with 20 ml. of conc.

sulphuric acid and 50 ml. of conc. nitric acid (the amount usually employed in a destruction) and then proceeding as described above. The solution, after oxidation with potassium periodate, was diluted to 250 ml., thereby giving a solution containing 0·002 mg. of manganese per ml. Ten to 30 ml. of this solution were diluted to 50 ml., the colour was re-developed, and thus tintometer readings were obtained for concentrations of manganese from 0·02 to 0·06 mg. in the 50 ml.

A confirmatory series of determinations was carried out by the ashing process. One-gram samples of the teas, weighed into small silica basins and moistened with 1 to 2 ml. of conc. sulphuric acid were ashed at dull red heat in a muffle furnace. The residual white ash was dissolved in dilute sulphuric acid (15 ml. of conc. acid per 100 ml. of water), and filtered, the filter-paper was ignited, and the residue, if any, was dissolved in about 10 ml. of the diluted sulphuric acid; the solution was filtered into the main filtrate, which was then oxidised with potassium periodate. Tintometer readings were taken after suitable dilution and re-development as before.

TABLE I

TEAS

Description.. ..	Ceylon O.P.	Ceylon B.O.P.	Assam B.O.P.	Dooars B.O.P.	Malaya B.O.P.	Travancore B.O.P.*	Japan Black	Keemun China
Moisture, per cent. ..	6·1	6·6	5·4	5·5	6·1	5·3	6·0	6·5
Caffeine, per cent. (on dried tea)	3·35	3·54	4·23	4·79	4·30	3·13	2·45	3·18
	3·27	3·47	4·18	4·80	4·43	3·21	2·43	3·27
	3·25	3·55	4·26	4·83	—	3·21	—	—
	—	—	—	4·80	—	—	—	—
Manganese, per cent. (on dried tea)								
Wet oxidation	0·0292	0·0271	0·090	0·0145	0·0184	0·0174	0·085	0·047
	0·0292	0·0269	0·089	0·0145	0·0182	0·0173	0·084	0·047
	—	—	0·090	—	0·0182	0·0175	—	—
Low temp. ashing ..	0·0291	0·0272	0·090	0·0147	0·0180	0·0172	0·083	0·048
High-temp. ashing	—	—	—	—	—	—	—	—

TEAS—*continued*

Description	Sylhet B.O.P.	Java B.O.P.	Sumatra B.O.P.	Nyasaland B.O.P.	Nyasaland Fannings	Kenya B.O.P.	Assam B.P.
Moisture, per cent.	5·2	6·0	5·7	5·8	5·5	5·8	5·3
Caffeine, per cent. (on dried tea)	3·64	3·47	3·70	2·71	2·85	2·84	4·68
	3·66	3·42	3·72	2·74	2·90	2·91	4·74
Manganese, per cent. (on dried tea)							
Wet oxidation	0·053	0·0080	0·0145	0·089	0·057	0·138	0·031
	0·054	0·0079	0·0146	0·087	0·056	0·137	0·032
Low temp. ashing ..	0·052	0·0082	0·0148	0·089	0·057	0·135	0·032
High temp. ashing ..	—	—	—	—	—	—	0·031

* O.P. = Orange Pekoe; B.O.P. = Broken Orange Pekoe; B.P. = Broken Pekoe.

A calibration curve for this procedure was obtained by evaporating 5 ml. of the manganous sulphate solution (0·1 mg. of manganese per ml.) to dryness, adding 1 to 2 ml. of conc. sulphuric acid, and heating in the muffle-furnace at dull red heat for 3 to 4 hours. The residue was dissolved in the dilute sulphuric acid,

the manganese was oxidised with potassium periodate, and the tintometer readings were taken as before.

It was found that heating in the muffle at bright red heat or treatment of the manganous sulphate directly with potassium periodate gave readings which agreed exactly with those obtained by the procedures previously described. Hence no loss in manganese occurs during either the wet oxidation or the ashing treatment.

In one experiment a sample of tea was ashed at the full muffle temperature, and the result agreed, within the limits of experimental error, with those obtained by the ordinary low-temperature ashing.

Caffeine.—The caffeine-content of the tea was determined by the Bailey and Andrew method.[2] The nitrogen-content of the impure residue of caffeine was determined by the usual Kjeldahl procedure, and the amount of caffeine was calculated from N × 3·464.

The results (Table I) are expressed as percentages on the dried tea, the moisture-content being determined by drying 1 to 2 g. at 100° C. Preliminary experiments showed that two hours' drying was sufficient to expel all the moisture.

COFFEE.—*Manganese.*—The manganese-content of coffee was determined by the ashing procedure, using 5 g. quantities of the coffee beans, broken in a porcelain mortar and mixed as thoroughly as possible. It was found that determinations on the powder obtained by grinding the beans in an ordinary coffee-mill usually gave higher results. This was found to be due to minute particles from the blades of the mill (filings of which were found to contain manganese). It was noticeable that with coffee beans which were brittle, and hence easily powdered, the results on the powdered samples agreed with those on the broken beans.

Some manganese determinations were carried out on the de-caffeinated residue obtained after chloroform extraction of the finely-ground coffee. These were found to agree, within the limits of experimental error, with those obtained on the original powder. Hence practically no manganese was extracted with the caffeine.

Caffeine.—The caffeine-content of coffee was determined on the finely-ground samples by the Gorter method. It was found that the original procedure[3] gave low and widely discordant results, and hence the caffeine was extracted from the fatty residue by boiling with water instead of treatment with hot water. This modification has also been described by Fox and Sageman.[4]

In the two determinations the nitrogen figure obtained from a Kjeldahl determination on the aqueous extract of the fatty residue was found to give a caffeine-content higher than that obtained from a Kjeldahl determination on the impure caffeine obtained by chloroform extraction of the aqueous extract.

To facilitate the extraction of caffeine from the fatty residue, the following procedure is suggested. About 10 g. of the dried, finely-ground coffee are extracted four times in a Soxhlet extractor with sodium-dried ethyl ether, which removes almost all the fat but only about 10 per cent. of the caffeine; the ethereal extract is evaporated to dryness, and the residue is extracted with boiling water in the usual way. As there is only a small proportion of the caffeine present in this extract, no great error can ensue through incomplete extraction with water. The de-fatted coffee in the Soxhlet thimble is moistened with about 5 ml. of water,

after removal of the last traces of ether in a water-oven, and extracted with chloroform. The extract is then treated as before. As there is only a very small amount of fat present, the extraction of the caffeine is greatly facilitated. The combined aqueous extracts are extracted with chloroform, and the nitrogen of the impure caffeine is determined by the Kjeldahl method in the usual manner.

The results (Table II) are expressed as percentages of the dried coffee, the moisture-content being determined as with tea, by drying 1 to 2 g. of the finely-ground coffee at 100° C. for periods of 2, 4 and 6 hours; from the results obtained it was clear that 2 hours were sufficient.

TABLE II

COFFEES

Description	Mocha	Costa Rica	Malabar	Santos	Kenya	Mysore
Moisture, per cent.	6·8	7·4	6·5	6·8	6·8	6·9
Caffeine, per cent. (on dried coffee)						
Original Gorter method (fatty residue extracted with hot water)	0·96	1·10	1·32	0·92	—	—
	0·93	0·76	1·26	0·88	—	—
	0·89	—	1·32	0·82	—	—
	—	—	1·26	—	—	—
Modified Gorter method (fatty residue extracted by boiling with water)	1·05	1·21	1·33	0·99	1·09	1·28
	1·06	1·22	1·34	1·01	1·13	1·28
	1·10	1·23	1·35	1·02	1·14	1·25
Modified Gorter method (no $CHCl_3$ extn. of aqueous extract of fatty residue)	1·14	—	—	—	1·17	—
Modified Gorter method (after separation of fat by extraction with dry ether)	—	—	—	0·99	—	—
Manganese, per cent. (on dried coffee)						
On broken beans	0·00131	0·00131	0·00181	0·00175	0·00324	0·00174
	0·00131	0·00132	0·00186	0·00176	0·00319	0·00173
	0·00129	0·00133	0·00186	0·00176	0·00318	0·00171
Finely-ground powder ..	0·00137	0·00149	0·00181	0·00187	—	0·00171
	0·00147	0·00150	0·00183	0·00186	—	—
	0·00149	0·00151	0·00184	0·00184	—	—
	0·00152	0·00151	0·00186	0·00183	—	—
On de-caffeinated powder ..	0·00140	0·00148	0·00178	—	—	—
	—	0·00149	—	—	—	—

The results for caffeine and manganese showed that there is a general tendency towards an inverse relationship between the manganese and caffeine contents of teas. No such relationship, however, exists with coffee, for which the caffeine-contents are relatively constant. It is worthy of note that African teas have, in general, a higher manganese-content than Indian. The sample of Kenya coffee had also a relatively high manganese-content.

We wish to express our thanks to Mr. A. A. Eldridge for helpful advice, and to Messrs. J. Lyons & Co. (per Dr. L. H. Lampitt), to Messrs. Gow, Wilson and Stanton, and to the Director of the Imperial Institute for supplying samples of teas and coffees.

REFERENCES

1. A. Broek and L. K. Wolff, *Acta Brevia Neerland. Physiol., Pharmacol., Microbiol.*, 1935, **5**, 80.
2. Association of Official Agricultural Chemists, *Methods of Analysis* (3rd Ed.), Washington, 1930, p. 155.
3. K. Gorter, *Annalen*, 1908, **358**, 327; Abst., ANALYST, 1908, **33**, 124.
4. J. J. Fox and P. J. Sageman, *Allen's Commercial Organic Analysis*, Vol. **7**, p. 383.

CHEMISTRY DEPARTMENT
ROYAL COLLEGE OF SCIENCE
LONDON, S.W.7

June, 1939

Observations on the Use of Potassium Chromate as Indicator for the Titration of Chlorides with Silver Nitrate

BY A. J. BERRY, M.A., AND J. E. DRIVER, M.A., PH.D., M.SC., F.I.C.

MOHR'S original method for the determination of chlorides with silver nitrate has been the subject of numerous investigations, and, although the method is perhaps less widely used at the present time than formerly, on account of the rapidly extending use of adsorption indicators, it is still a standard method of analysis and likely to remain so for many years to come. Modern investigations on Mohr's method have been chiefly concerned with two factors, namely, the quantity of indicator which should be used in order to work the method with the maximum degree of accuracy, and the extent of the permissible deviations from strict neutrality of the solution.

In the older literature considerably varied quantities of potassium chromate were recommended for determining the end-point, but perhaps the most generally used quantity was of the order of 1 ml. of a one per cent. solution for a total volume of 100 ml. of liquid when solutions of $N/10$ concentration were analysed. Kolthoff,[1] having regard to the ionic products of silver chloride and silver chromate, recommended 1 ml. of a 1/3rd molar solution of potassium chromate per 100 ml. of liquid, corresponding to a chromate ion concentration of $3{\cdot}3 \times 10^{-3}$ molar. Van Urk,[2] as the result of similar reasoning, concluded that the minimum chromate ion concentration should be $0{\cdot}7 \times 10^{-3}$ molar and that the maximum concentration should not exceed 15×10^{-3} molar. It will be noted that van Urk's minimum concentration exceeds that which would be given by 1 ml. of a one per cent. solution of potassium chromate per 100 ml. of solution, the latter giving a chromate ion concentration of $0{\cdot}5 \times 10^{-3}$ molar.

Acid solutions of chlorides are most usually neutralised with calcium carbonate when Mohr's method is employed. Kolthoff (*loc. cit.*) investigated the limits of acidity which he considered permissible for accuracy. In his text-book[3] he summarised the best conditions for working the process, recommending the use of 1 to 2 ml. of a 5 per cent. solution of potassium chromate per 100 ml. of final volume of liquid, and giving the limits of the *p*H value of the solution as between

6·5 and 10·5. Acid solutions should be brought to this reaction by the use of borax or sodium bicarbonate. It may be added that Doughty[4] carried out a few experiments on the titration of acid solutions of chlorides which were buffered with sodium acetate to a *p*H value of 5·5, and he stated that accurate results were obtainable under these conditions.

Although much attention has been given to the concentration of the indicator and the relative acidity of the solution, very few, if any, writers have made any remarks on the alkaline properties of the indicator itself. Potassium chromate in solution is sufficiently hydrolysed to show a definitely alkaline reaction. Numerous investigations have been made, by physical methods, on the properties of solutions of chromates, of which mention may be made of Britton's experiments on the electrometric titration of chromic acid[5] and on the precipitation of basic chromates.[6] In this second paper the *p*H of potassium chromate in $M/100$ concentration is stated to be 9·25. It follows that the addition of potassium chromate to any chloride solution within certain limits of acidity will necessarily diminish its hydrogen ion concentration. The amount of change due to the quantity of indicator suitable for purposes of titration may be of the order of 1 to 2 *p*H units. If the limits of acidity of a chloride solution that can be titrated with accuracy by Mohr's method are to be clearly defined, either the indicator must be adjusted to *p*H 7 before it is added to the solution, or the *p*H of the solution containing the indicator must be determined before the titration is carried out. Solutions of potassium chromate can be adjusted to *p*H 7 by careful dilution with nitric acid, or, alternatively, with a solution of potassium dichromate. A solution of a mixture of potassium chromate and potassium dichromate has considerable buffering properties, as may be seen by a study of Britton's titration curves (*loc. cit.*).

There appears to be an impression among many chemists that ammonium chloride should not be determined by Mohr's method, but that Volhard's process should be used. This idea seems to be based partly upon the slight acid hydrolysis of the salt, and partly upon the influence of ammonium salts on the solubility of silver chromate. The *p*H of solutions of ammonium chloride of suitable concentration for volumetric determination is usually about 5. As regards the influence of ammonium salts on Mohr's process, Kolthoff (*loc. cit.*[3]) remarks that pure ammonium salts of strong acids are without influence upon the accuracy of the method, provided that the *p*H of the solution under these conditions is maintained within the limits of 6·5 and 7·2. At lower hydrogen ion concentrations ammonia is liberated, with disastrous effects on the accuracy of the process. It was primarily with the object of ascertaining the quantitative effects of acidity and of the presence of ammonium salts on Mohr's method that the experiments described in this paper were carried out. Some experiments were also made on the titration by Mohr's method of hydrochloric acid neutralised with calcium carbonate, with the object of effecting a comparison with results obtained by direct quantitative neutralisation with sodium carbonate.

Experimental

Effect of Acidity on Mohr's Process.—Titrations of potassium chloride with silver nitrate were carried out in the following way:—A weighed quantity of

silver nitrate, slightly in defect of the amount of potassium chloride solution to be added, was dissolved in 25 ml. of CO_2-free water, and a measured volume of $N/100$ nitric acid was added. Then 63·74 ml. of approximately $N/10$ potassium chloride solution were added from a Stas pipette, followed by 2 ml. of a 1·5 per cent. potassium chromate solution which had been previously adjusted to *p*H 7·0 by addition of nitric acid. The titration was then completed by running in $N/20$ silver nitrate solution from a burette. The *p*H values were determined with the aid of a Lovibond comparator, solutions prepared in a precisely similar manner but with omission of the silver nitrate being used.

The results, given in Table I, are expressed in the form of weight of silver nitrate required for 63·74 ml. of potassium chloride solution. The figures given for solutions in the neighbourhood of neutrality are the average of several titrations, with a maximum deviation from the average of less than 1 part per 1000; at the higher acidities the plotted results showed that duplication was unnecessary. The first result recorded was obtained with unneutralised indicator of the same concentration, and the alkalinity is due to hydrolysis of the potassium chromate. Below *p*H 3·8 no satisfactory end-point was obtainable.

The effect of increasing acidity on the titration figures is seen more clearly from a graph, in which *p*H values are plotted against weights of silver nitrate.

TABLE I

*p*H of solution	Weight of silver nitrate required g.
7·8	1·0761
7·0	1·0763
6·2	1·0784
5·4	1·0797
5·0	1·0826
4·2	1·0941
3·8	1·1182
3·4	—

These results may be compared with the calculated quantity of silver nitrate and with the results of titrations in which phenosafranine was used as adsorption indicator.

Calculated weight of $AgNO_3$ = 1·0804*; average result with phenosafranine = 1·0754.

TITRATION OF AMMONIUM CHLORIDE, AND EFFECT OF EXCESS OF AMMONIUM SALTS.—These titrations were carried out in a manner similar to those previously described for potassium chloride, but with the use of approximately $N/10$ ammonium chloride solution (in quantities of 63·74 ml., measured from a Stas pipette). In order to study the effect of excess of ammonium salts, measured volumes of N solutions of ammonium nitrate or of ammonium acetate were added prior to completion of the titration with $N/20$ silver nitrate solution. The results recorded in Table II are in each instance the average of two or more determinations with a deviation from the average of less than 1 part per 1000.

* A hypothetical figure, based on the assumption of 100 per cent. purity for both reactants.

TABLE II

	Conditions of experiment	*p*H of solution	Weight of silver nitrate required g.
1	Ammonium chloride solution, with no additional ammonium salts; unneutralised chromate indicator	6·9	1·1126
2	As (1), but with neutralised chromate	6·4	1·1126
3	As (1), but with addition of 1 mol. of NH_4NO_3 per mol. of NH_4Cl	6·8	1·1159
4	As (1), but with addition of 5 mols. NH_4NO_3 per mol. of NH_4Cl	6·6	1·1194
5	As (1), but with addition of 1 mol. ammonium acetate per mol. of NH_4Cl	6·9	1·1164
6	As (1), but with addition of 5 mols. of ammonium acetate per mol. of NH_4Cl	7·0	1·1319

These results may be compared with the calculated quantity of silver nitrate (100 per cent. purity of both reactants being assumed) and with titrations in which phenosafranine was used.

Calculated weight of $AgNO_3$ = 1·1088 g.*; average result with phenosafranine = 1·1118 g.

TITRATION OF HYDROCHLORIC ACID.—A weighed quantity of silver nitrate was dissolved in water, and 63·74 ml. of approximately $N/10$ hydrochloric acid were added, followed by 2 ml. of unneutralised chromate indicator. An excess of calcium carbonate was then added, and the liquid was shaken and allowed to stand for about two minutes. The *p*H of the solution at this stage varied between 5·8 and 6·4. The titration was completed with $N/20$ silver nitrate solution. The results of four determinations showed a maximum deviation from the average of just over 1 part per 1000. The figures in Table III show how the results compare with those obtained by other methods. For the sodium carbonate titrations, weighed quantities of the carbonate were treated with 2 × 63·74 ml. of the acid, and the titration was completed by running acid from a burette, bromophenol blue or methyl orange being used as indicator. This gave, for calculation, a titration figure of the order of 140 ml.

TABLE III

Method	Average result (g. of HCl per litre)
Mohr's	3·661
Phenosafranine	3·655
Sodium carbonate	3·653

SUMMARY AND CONCLUSIONS.—At the outset it may be noted that the quantity of potassium chromate that was used in our experiments would produce in the solutions a concentration of chromate ions of about $1·5 \times 10^{-3}$ molar. This particular concentration is well within the limits laid down by van Urk, and it may be doubted if any advantage is to be gained by working towards the

* A hypothetical figure, based on the assumption of 100 per cent. purity for both reactants.

upper limit set by him, on account of the very strong colour of the chromate ions. In any event the experimental error was less than one part in one thousand.

When neutral alkali chlorides are titrated by Mohr's method, highly accurate results are obtained, and, up to an acidity of *p*H 5·5, the error does not exceed 3 parts per thousand. At higher acid concentrations, however, the consumption of silver nitrate increases very appreciably. Thus at *p*H 3·8 the results are about 4 per cent. too high, and at *p*H 3·4 no definite end-point was obtainable.

In the titration of ammonium chloride by Mohr's process, the addition of the chromate indicator diminishes the acidity of the solution to a value well within the limits in which the maximum degree of accuracy of titration can be realised. The consumption of silver nitrate is only slightly higher than when phenosafranine is used as indicator, the difference being less than 1 part per thousand. That the presence of ammonium salts has a slight, but decided, effect upon the accuracy of the process is shown by the results obtained when ammonium nitrate was present. Thus when the molar ratio of ammonium nitrate to chloride was 5:1, the consumption of silver nitrate was increased by about 7 parts per thousand. The effect of ammonium salts of weak acids, such as ammonium acetate, is more pronounced. When the molar ratio of acetate to chloride was 5:1, the increase in consumption of silver nitrate was found to be nearly 2 per cent.

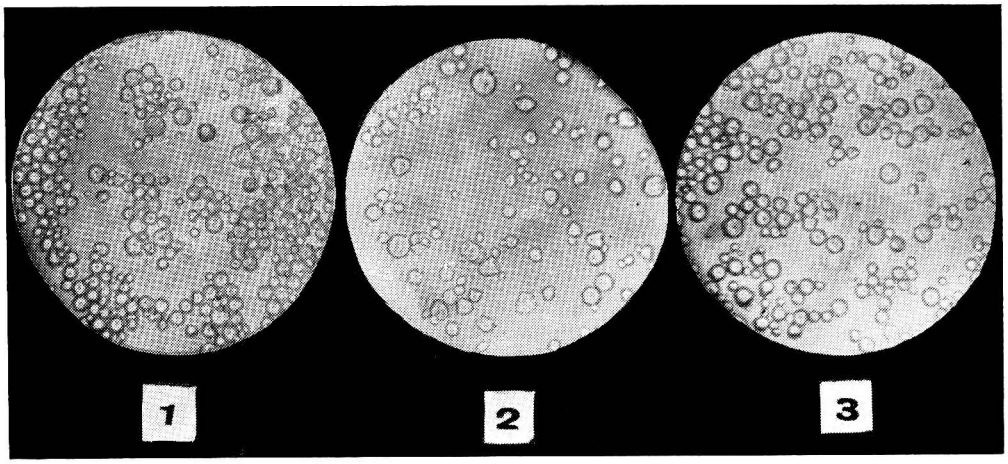
When hydrochloric acid is neutralised with calcium carbonate and then titrated by Mohr's method, the result is higher by about two parts per thousand than when the acid is determined by neutralisation with sodium carbonate. The *p*H value of hydrochloric acid treated in this way (*i.e.* with excess of calcium carbonate) is about 6, but it must be borne in mind that even the purest precipitated calcium carbonate commercially obtainable may contain about 0·1 per cent. of alkalis.

References

1. I. M. Kolthoff, *Z. anal. Chem.*, 1917, **56**, 498.
2. H. W. van Urk, *id.*, 1925, **67**, 281.
3. I. M. Kolthoff, *Massanalyse*, II, p. 224.
4. H. W. Doughty, *J. Amer. Chem. Soc.*, 1924, **46**, 2707.
5. H. T. S. Britton, *J. Chem. Soc.*, 1924, **125**, 1572.
6. —— *id.*, 1926, 125.

The Chemical Laboratory
University of Cambridge

July 15, 1939



1 Tapioca starch　　2 Sweet potato starch　　3 Linseed starch

Magnification ×140

Notes

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

THE STARCH OF IMMATURE LINSEED

IT is frequently necessary to examine linseed cake meals for adulterants, and, as the starch found in mature linseed is negligible, a positive iodine reaction is the prelude to a microscopical examination to identify the admixture.

For research purposes Mr. C. Robertson Louden grew linseed from imported seed in the wet summer of this year and handed to me, from his crop, some pods containing fully-grown but immature seeds. These seeds contained starch granules indistinguishable from those of tapioca starch, but slightly smaller than those of sweet potato starch.

As there appears to be no record of linseed starch in the literature, the accompanying photo-micrographs, taken by Mr. C. F. Waters in this laboratory, may be of interest.

In preliminary experiments Messrs. Louden and Antrobus have found that hydrocyanic acid is not evolved from linseed containing starch, but that as the starch is replaced by oil the seeds become cyanogenetic (*cf.* ANALYST, 1939, 681).

F. ROBERTSON DODD

THE LABORATORY
59, VICTORIA STREET
LIVERPOOL, 1

NOTE ON THE USE OF HYPOCHLORITE IN WATER ANALYSIS

R. BUYDENS (*Water Pollution Research*, 1936, **9** [No. 2], 51, par. 193) suggests that animal and vegetable organic matters in water may be differentiated by their relative action on potassium permanganate and sodium hypochlorite. This method, with slight modification, was adopted in the following determinations:

Permanganate Figure.—Ten ml. of $N/80$ potassium permanganate solution and 5 ml. of sulphuric acid (1 in 4) are added to 100 ml. of the water in a 500-ml. conical flask, the mixture is heated to boiling in 5 minutes, and boiling continued for another 10 minutes. After cooling, potassium iodide is added and the liquid is titrated with $N/250$ thiosulphate solution (1 g. of sodium thiosulphate per litre), starch being used as indicator.

Sodium Hypochlorite Figure.—Ten ml. of $N/10$ sodium hypochlorite solution are added to 100 ml. of the water in a 500-ml. conical flask, the mixture is heated to boiling, in 5 minutes, and boiling is continued for another 10 minutes. On cooling, 2 ml. of 10 per cent. potassium iodide solution and 10 ml. of strong hydrochloric acid are added, and the liquid is titrated with $N/40$ thiosulphate solution, α-naphthoflavone (0·1 per cent. in alcohol) being used as indicator.

In both titrations the results are expressed in parts of oxygen absorbed per 100,000 parts of water.

The liquids used in the experiments were made by adding vegetable and animal substances to tap water in such proportions as to give an oxygen absorbed

($KMnO_4$) figure in 4 hours at 80° F. of approximately 0·25 part per 100,000 for each solution.

	Permanganate absorbed		Hypochlorite absorbed	Ratio
	in 4 hrs. at 80° F.	in 10 mins. at b.p.	in 10 mins. at b.p.	NaOCl:Permanganate (at b.p.)
Vegetable				
Peat	—	0·50	1·11	2·2 : 1
Leaf mould	0·28	0·48	0·92	1·9 : 1
Tea leaves	0·28	0·46	0·80	1·7 : 1
Pea	—	0·50	0·50	1·0 : 1
Animal				
Urine	0·26	0·52	4·4	8·4 : 1
Effluent	0·23	0·42	3·1	7·4 : 1

Thus the ratio between the two figures in presence of vegetable matter does not exceed 2, whereas that from animal sources lies between 5 and 8. These ratios obviously apply to drinking waters and should be particularly useful when an opinion has to be passed on waters of doubtful quality.

In order to give the process a more stringent test, an attempt was made to produce a liquid containing no animal matter, but having a ratio of albuminoid ammonia: oxygen absorbed suggestive of the presence of animal matter. This liquid was prepared by soaking bran with weak saline and filtering. The filtrate gave a positive biuret reaction, indicating the presence of protein derivatives. After adequate dilution it gave the following figures:

	Parts per 100,000
Albuminoid ammonia	0·045
Permanganate demand in 4 hours at 80° F.	0·14
,, ,, ,, 10 mins. at b.p.	0·73
Hypochlorite ,, ,, 10 ,, ,, ,, ...	0·75

The first two figures, interpreted in the usual manner, would lead one to assume the presence of animal matter, whereas consideration of the last two figures avoids such a fallacy.

F. DIXON
D. C. JENKINS

THE COUNTY LABORATORY
STAFFORD

August, 1939

Official Appointments

THE Ministry of Agriculture and Fisheries has approved the following appointments:

H. C. L. BLOXAM, F.I.C., as Agricultural Analyst for the County Boroughs of Gateshead, South Shields, Sunderland and Tynemouth, *vice* Dr. J. T. Dunn (deceased) (June 28th).

J. L. WILSON, M.Sc., F.I.C., as Deputy Agricultural Analyst for the County Borough of Burnley (June 28th).

Legal Note

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

ADULTERATION OF "APPEAL-TO-COW" SAMPLES OF MILK

It may be of interest to other analysts to learn that milk may actually be watered under the eyes of the inspector. A case arose out of two samples purchased under the Food and Drugs Act in February, 1939. On the basis of the freezing-point depressions the informal and formal samples were certified to contain at least 3·5 and 2·3 per cent. of added water, respectively. Two days later, at the request of the farmer, the herd of ten cows was milked in the presence of two inspectors. The morning milk was found to be genuine, whilst the sample of evening milk contained 5·2 per cent. of added water. There was no question of a leaking cooler, and it was therefore suggested that I should accompany the two inspectors and take informal samples from each cow. The lighting conditions were poor, and as the inspector followed the farmer into the shed, he saw him pause, as if to adjust his apron. Then, as the farmer sat down to milk, he swung the pail, and the inspector heard a slopping sound, but before he could get to the farmer, milking had started, and although the pail had been dried previously, a considerable quantity of milky fluid was observed. The complete sample was calculated to contain 11·7 per cent. of added water. On the afternoon of the same day other samples were taken, and one was found to contain 9·4 per cent. of added water. The circumstances connected with the collection of this sample were highly suspicious, in that the farmer, while bending over the pail, was seized with a fit of coughing, and a gurgling sound, similar to that of liquid being poured from a bottle, was heard. Later a flat bottle was found concealed in the folds of the farmer's apron when it was removed. Further, the comparison of the analytical figures of this sample with those obtained by the chemists for the defence showed that by some means or other a genuine sample had been substituted and sent to them. This second portion was received in a sealed condition and no evidence of tampering could be seen in the bottle itself. On the following morning further samples from the cows alleged to have given the two watered samples were taken, and these were found to be genuine.

As the original sample contained only 2·3 per cent. of added water, as calculated from the Milk Regulations standard, it is probable that a caution might have been found sufficient, but the subsequent behaviour of the farmer resulted in a prosecution, and a fine of £50 with 10 guineas costs was imposed, two previous convictions having been recorded.

F. E. Needs

Notes from the Reports of Public Analysts

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

CITY AND COUNTY OF KINGSTON-UPON-HULL

Report of the Public Analyst for the Year 1938

Of the 2376 samples submitted under the Food and Drugs Act, 1376 were purchased formally.

Pork Dripping.—Four samples contained from 10 to 31 per cent. of water in the form of gravy, without label or declaration, in contravention of the local agreement with the Master Butchers' Association. The vendors were cautioned.

Ice-Cream.—The fats in two samples contained from 40 to 50 per cent. of vegetable fats. Hence it is desirable that any standard for the composition of ice-cream should take account of the fact that milk-fat is no longer the only source of fat in many of these confections.

The bacteriological examination of these products continued to cause misgiving. Of 56 samples examined, 40 were not satisfactory; more than half of these contained bacteria in excess of 500,000 per 1 ml., and also excessive numbers of *B. coli* (present in 0·1 ml.). The Medical Officer and I, in a joint report on ice-cream, recommended that standards and definitions for these products should be set up, and that consideration should also be given to the practicability of fixing bacteriological standards of purity. This report has been sent to the Ministry of Health.

Atmospheric Pollution Observations.—The results obtained during the year show that the amount of pollution, as judged by the deposit gauges, was practically stationary over the years 1936–1938. The average amount of solid matters deposited from the air (solid deposit and in solution in rain water) over the whole City in one year may be taken to be about 200 tons per square mile.

The daily average of sulphur dioxide in the air of the central area of the City is 0·03 volume per million during the summer months and 0·06 volume per million in winter. These figures may be compared with those of certain other areas for the year 1937–1938 (April to March): Hull, 0·06; Leicester, 0·10; London (Westminster), 0·14; Sheffield, 0·14 volume per million per day.

The amounts of sulphur gases (mg. of SO_3) per 100 sq. cm. of exposed surface of lead peroxide per day were as follows:—Maximum (January and December), 3·7; minimum (June), 1·4; average, 2·4.

The greatest amount of suspended impurities in the air was again recorded in November, when the figure was 51 mg. per 100 cubic metres. This result is in excess of the amounts found in the two previous years.

Ultra-Violet Light Observations.—The units of fading of a standard methylene blue solution recorded during the year varied from $\frac{1}{4}$ to $1\frac{1}{2}$ as the daily average during each month. Comparative figures for Bridlington and Scarborough are:—Bridlington, $\frac{1}{4}$ to $1\frac{1}{2}$; Scarborough, $\frac{1}{2}$ to $2\frac{3}{4}$ units.

Chemical Evidence of Safe-breaking.—In this case material from the lock of the safe consisted of a brown fibrous cloth of wool and hair, with vari-coloured particles of plasticine, and the remains of an explosive substance containing ammonium nitrate and a nitrated compound of glycerol. This was incorporated in an absorbent material of the nature of oat-bran. Fabrics from a position near the area of explosion were torn to shreds and were charred or scorched by fire.

POISONING WITH PHENO-BARBITONE.—In a case of suicide pheno-barbitone was isolated in small quantities from the stomach contents (0·5 grain), liver (2·3 grains), and kidneys (0·3 grain). The pheno-barbitone crystals recovered had m.p. 173° C. Some 5-grain tablets examined in connection with this case consisted of the sodium compound of pheno-barbitone. ARNOLD R. TANKARD

WORCESTERSHIRE COUNTY COUNCIL

ANNUAL REPORT OF THE COUNTY ANALYST AND BACTERIOLOGIST

OF the 858 samples submitted under the Food and Drugs Act, 387 were purchased formally.

GUARANTEES OF FERTILISERS AND FEEDING STUFFS.—In my opinion, failure to give the statutory guarantee is, in most instances, more than a technical offence. Thus, in the guarantees for phosphatic fertilisers "phosphates" are guaranteed instead of phosphoric acid, and "ammonia" instead of nitrogen for nitrogenous fertilisers. Since 10 per cent. of phosphoric acid is equivalent to 21·8 per cent. of "phosphates" and 10 per cent. of nitrogen to 12·1 per cent. of ammonia, it is obvious that this kind of evasion of the Act gives the seller an advantage. Not all farmers are sufficiently versed in chemistry to watch for and appreciate these distinctions when buying fertilisers. These practices will continue until a prosecution is brought as a warning to vendors. Hitherto, however, the Minister of Agriculture has not been disposed to sanction such a course. H. E. MONK

Ministry of Health

SALE OF FOOD AND DRUGS

ABSTRACT OF REPORTS OF PUBLIC ANALYSTS FOR THE YEAR 1938

THE number of samples of foods and drugs reported on by Public Analysts during 1938 was 150,576, a slight decrease on the number for the previous year (151,370) (*cf.* ANALYST, 1938, **63**, 816). Of these, 8433 or 5·7 per cent. were reported against.

PRESERVATIVES.—Contraventions of the Public Health Regulations were responsible for 430 adverse reports, of which 46 related to sausages. Table jellies contained benzoic acid, and barley, pickles and potted and other meats contained sulphur dioxide. Samples containing preservative in excess of permitted quantities included jam, sausages, dried fruits, beer, non-alcoholic wines and fruit juices. Boron preservative was present in cream, butter and sausages, in one sample of milk and in one of fresh meat.

MILK.—Of 80,025 samples (excluding 1494 "appeal-to-cow" samples with 620 reported as below standard), 6141 were reported against. In one case of successful prosecution a sample of milk contained 25 per cent. and in another the samples had up to 40·1 per cent. of added water. Also, a few samples contained dirt.

CONDENSED AND DRIED MILK.—Thirty samples of condensed and 4 of dried milk were reported against.

CREAM.—Of 27 samples of cream reported against, 11 contained boron preservative.

BUTTER AND MARGARINE.—Of 104 samples of butter reported against, 87 contained water in excess of 16 per cent., and one was also very rancid; 6 contained a large proportion of margarine, whilst 13 others consisted partly, and one wholly, of margarine; 3 contained boron preservative.

LARD AND OTHER FATS.—Eighteen samples of lard consisted wholly or partly of other fats, 3 samples contained water (1·4, 9·4 and 11 per cent. respectively), and one had excessive acidity. Most of the 35 samples of suet adversely reported on contained undeclared or excessive proportions of rice flour or other starchy matter, whilst 9 samples of dripping contained excess of water and 2 contained free fatty acids; one lard contained 30 per cent. of "nut" oil.

CHEESE.—A low fat-content was responsible for most of the 79 samples of cheese reported against. One sample of wrapped cheese was infested with acari and fungus, one was contaminated with crystals of sodium phosphate, one with crystals of lactose hydrate, and one contained 3·12 grains of tin per lb.

BREAD AND FLOUR.—Four samples of bread and 11 of flour were reported against. One flour contained 25 per cent. of potato starch and 2 samples of self-raising flour contained excess of sodium bicarbonate, whilst 2 ordinary flours were sold as self-raising flours.

JAM AND MARMALADE.—Many of the 165 samples reported against were deficient in fruit or soluble solids. Some samples of strawberry, of blackcurrant, and of raspberry jam were found to contain only 3 per cent. of the named fruit, and 63 samples contained excessive proportions of sulphur dioxide.

VINEGAR.—The chief trouble with the 152 samples of vinegar unfavourably reported on was a deficiency of acetic acid or a sale of artificial vinegar as "malt" or "table" vinegar.

SPIRITS AND BEER.—A deficiency of proof spirit was reported in 45 samples of whiskey, 32 of gin, 18 of rum and 8 of brandy, and one sample of whiskey was also stated to be mixed with wine, whilst a sample of rum contained 33·72 per cent. of ginger wine. Of 597 samples of beer, 66 were reported against, one sample for containing zinc and 62 for contamination with lead.

MISCELLANEOUS ARTICLES OF FOOD.—The 36,000 samples of other foods included a wide variety, of which only a few can be mentioned. Most of the 76 samples of canned fish reported against were condemned on account of contamination with tin, and tin was also responsible for the adverse reports on 41 samples of sugar, canned fruits, vegetables and soups, whilst lead was present in 19 samples of sardines and 10 of curry powder, and copper in a number of articles including sweets and canned tomato products. Zinc was present in ice-cream, one sample of dried apple rings and one of canned spinach, and arsenic in 2 samples of dried parsley, one of granulated gelatin and one of apples. Seventy-nine samples of chocolate rolls and other chocolate cakes were reported as deficient in cocoa matter, 56 of 69 samples sold as bread and butter proved to be bread and margarine, and 13 bread and a mixture of butter and margarine. One sample of cocoa contained 50 per cent. of cane sugar, one 6·75 per cent. of Epsom salts, one 1 per cent. of tapioca starch, and another starch and sand.

DRUGS.—Attention is called to the fact that several Food and Drug authorities took no samples of drugs during the year. Altogether 303 samples of drugs were found to be adulterated or not up to standard. Among these, a sulphur ointment contained no sulphur; iodine ointments and stainless iodine ointments were deficient in iodine; a sample sold as eucalyptus ointment contained 9 per cent. of methyl salicylate and no eucalyptus oil, and a sample of calomel ointment proved to be calamine ointment. Twenty-two samples of sweet spirit of nitre were reported against, mostly for deficiency of ethyl nitrite. Samples of ammoniated tincture of quinine were deficient in ammonia and/or quinine, and quinine cinnamon tablets were deficient in quinine sulphate. Bismuth and carbolic acid lozenges and aspirin tablets were unsatisfactory. Samples of camphorated oil, orange juice and halibut oil, sal volatile, magnesia, tincture of rhubarb, glycerin of borax (one sample consisted of 97 per cent. glycerin of phenol), linseed meal, blue pills, and hydrogen peroxide were reported against. A sample of paregoric consisted of orris root; two samples of ammoniated tincture of quinine were sold as dill water,

and a nerve tonic consisted only of cane sugar with a small proportion of cocoa, barley flour and milk powder. Six medicated wines were unsatisfactory, as were also samples of Seidlitz powders, cream of tartar, Glauber's salt, stomach powders, lime water and syrup of figs. Three prescriptions were found to be unsatisfactorily dispensed. D. G. H.

FOOD AND DRUGS ACT, 1938

TABLES OF COMPARISON*

THESE tables show: (i) The mode in which earlier enactments are dealt with by the Act. (ii) The sections of the Act and corresponding provisions in earlier Acts.

Table I is headed: Statement of Provisions in repealed Acts and corresponding Provisions, if any.

Table II is headed: Statement of Provisions and corresponding Provisions in earlier Acts.

The earlier Acts cited are: Market and Fairs Clauses Act, 1847; Public Health Act, 1875; Milk and Dairies (Consolidation) Act, 1915; Milk and Dairies (Amendment) Act, 1922; Public Health (London) Act, 1936. Reference is also made to Standard Clauses, Revised Edition, 1937.

STATUTORY RULES AND ORDERS

1939 No. 840

FOOD AND DRUGS, ENGLAND

PUBLIC ANALYSTS

THE PUBLIC ANALYSTS REGULATIONS, 1939, DATED AUGUST 1, 1939, MADE BY THE MINISTER OF HEALTH UNDER SECTIONS 66 (2) AND 69 (3) OF THE FOOD AND DRUGS ACT, 1938 (1 & 2 GEO. 6. C. 56).

101745.

Whereas it is provided by subsection (2) of section 66 of the Food and Drugs Act, 1938, that no person shall be appointed a public analyst unless he possesses either the prescribed qualifications or such other qualifications as the Minister of Health may approve;

And whereas it is provided by subsection (3) of section 69 of the said Act that the public analyst shall analyse as soon as practicable any sample sent to him in pursuance of that section and give to the person by whom it was submitted a certificate in the prescribed form specifying the result of the analysis:

Now therefore the Minister of Health in exercise of the powers conferred upon him by the said sections and of all other powers enabling him in that behalf hereby makes the following regulations:—

1. These regulations may be cited as the Public Analysts Regulations, 1939, and shall come into operation on the first day of October, 1939.

2. The Interpretation Act, 1889,† applies to the interpretation of these regulations as it applies to the interpretation of an Act of Parliament.

3. A person shall not be qualified to be hereafter appointed as a public analyst under the Food and Drugs Act, 1938, unless either (*a*) he already holds an appointment as public analyst, or (*b*) he is the holder of the Diploma of Fellowship or

* Pp. 18. To be obtained from H.M. Stationery Office, Kingsway, London, W.C.2. 1939. Price 3d. net.

† 52 & 53 Vict. c. 63.

Associateship of the Institute of Chemistry of Great Britain and Ireland and is also the holder of a certificate granted by that Institute after an examination conducted by them in the chemistry (including microscopy) of food, drugs and water.

4. The form set out in the schedule to these regulations is hereby prescribed as the form of certificate to be used by public analysts for the purpose of section 69 of the Food and Drugs Act, 1938.

SCHEDULE

FOOD AND DRUGS ACT, 1938

Form of Certificate of Public Analyst prescribed by the Minister of Health under Section 69 (3) of The Food and Drugs Act, 1938

To[1] .....

I, the undersigned, public analyst for the....., do hereby certify that I received on the.....day of..... 19...., from[2] .....(by registered post)[3], a sample submitted as a sample of....., for analysis which was marked[4]..... and weighed (or measured)[5].....

I further certify that I have analysed it, and as a result of my analysis I am of opinion that:—

it is a sample of.....

and/or

the constituents of the sample included the following substances in proportions as under:—

.....

.....

Observations[6]

.....

.....

As witness my hand this.....day of..... 19.... at.....

A.B.

.....

Notes.

[1] Here insert the name of the person submitting the sample for analysis.

[2] Here insert the name of the person delivering or sending the sample.

[3] Delete if inapplicable.

[4] Insert particulars of marking, *e.g.* date, number, etc.

[5] This may be left unanswered if the sample cannot be conveniently weighed or measured, or the weight or measurement is not material to the result of the analysis.

[6] Here the analyst may insert at his discretion his opinion whether the analysis indicates any addition, abstraction, or deficiency of any kind and whether the addition, abstraction or deficiency (if any) was for the purpose of rendering the article portable or palatable, or of preserving it, or of improving the appearance, or was unavoidable. He may also state whether the addition, abstraction or deficiency is in excess of what is ordinary, or otherwise, and whether it is or is not, injurious to health, and add any other observations he may wish to make. Where a sample of milk is found to be deficient both in milk fat and in other milk solids the analyst should indicate how much, if any, of the milk fat deficiency he considers to be due to abstraction, allowance being made for the effect of added water. In the case of a certificate regarding milk, or any other article liable to decomposition, the analyst should specially report whether in his opinion any change had taken place in the constitution of the sample that would interfere with the analysis.

Given under the official seal of the Minister of Health this first day of August, nineteen hundred and thirty-nine.

(L.S.)

R. STANTON,
Assistant Secretary, Ministry of Health.

Department of Scientific and Industrial Research

THE INVESTIGATION OF ATMOSPHERIC POLLUTION

REPORT ON OBSERVATIONS IN THE YEAR ENDED MARCH 31ST, 1938*

THE 24th Report on the Investigation of Atmospheric Pollution surveys the researches carried out and the results obtained by the 88 bodies (80 of which are municipal authorities) co-operating with the Department in the measurement of atmospheric pollution. During the last ten years the organisation covered by this co-operative effort has grown considerably in size. In 1928 the co-operating bodies operated 79 deposit gauges; to-day this number has increased to 124. In 1928 there were 6 automatic filters, while to-day 16 of these instruments are now in use. The 11 sets of volumetric sulphur apparatus and the 54 sets of lead peroxide apparatus now in use are new since 1928, these methods for measuring sulphur pollution having been standardised in the course of the investigation.

A comparison of the figures obtained with deposit gauges for the year under review with the average deposit for the 5 years ended 1932 shows that, for tar, 57 per cent. of the stations where such a comparison is possible have a marked reduction in the deposit, whilst 30 per cent. show an increase. The figures for the deposit of total solids show that 55 per cent. of the stations indicated record a marked decrease, whilst only 9 per cent. show a marked increase. Except that a smaller percentage of the stations showed an increase in tar deposit in the year 1936–1937, all the figures for 1937–1938 are rather better than the similar figures for the preceding two years. This is fairly satisfactory, but it is pointed out that the results are affected by rainfall, which was below the average in 1937–1938.

FOG HAZE.—The results from the stations where apparatus is used for measuring impurities suspended in the atmosphere show that the lowest concentration of sooty matter was found at Cardiff, and the next lowest at Kew Observatory. As in previous years, Cardiff has shown an extraordinarily clean air. Of the places where observations were made throughout the winter, Greenwich, with 65 per cent., had the greatest number of days with heavy smoke haze. Next followed Stoke with 59 per cent., and then London (Victoria Street) with 54 per cent. Westminster City Hall had 43 per cent., Glasgow 19 per cent., and Coventry 3 per cent., whilst Cardiff recorded none.

It appears that there is a tendency for smoke fogs to occur more frequently on Mondays, Tuesdays and Wednesdays than on the other days in the week. The reason for this is not obvious.

LEICESTER SURVEY.—The most important work that the Department of Scientific and Industrial Research is now carrying out as part of the co-operative scheme is the survey of atmospheric pollution in and around Leicester. This has been in progress for over a year. The work consists of three sections: the routine measurement of pollution, the study and analysis of the observations made, and the designing and testing of new experimental instruments for the measurement of pollution. The immediate object of the survey is to obtain information on the general occurrence and distribution of the commonest forms of atmospheric pollution in a typical city, with a view to providing a general basis for the wider interpretation of existing and future observations made by the co-operating bodies. The observations are being made with some 43 instruments placed in 13 selected sites in and near Leicester. The instruments include all those specified by the Department's Atmospheric Pollution Research Department as standard.

FORMATION OF FOGS.—The Report contains a section by Dr. J. S. Owens explaining the way in which fogs are formed. In this country fogs are caused

* H.M. Stationery Office, York House, Kingsway, London, W.C.2. 1939. Price: Report 2/- net; General Deposit Tables (issued separately) 4/6 net.

either by water droplets in the atmosphere or by smoke particles. The water droplets in a fog are only a few thousandths of a millimetre in diameter, and for this reason the sun, if visible, appears as a white disc. In a smoke fog particles are smaller, and the sun therefore appears red, because the smaller smoke particles scatter light of shorter wave-lengths but not light of the longer red wave-lengths.

It appears essential in the formation of fog that the air should contain very small particles on which the water condenses. It is believed that sea salt is a prolific source of such particles and that nitrous and sulphuric acids are also important sources. The other essential condition for the formation of a water fog is that the temperature of the air must be cold enough for this condensation to take place. A high wind may prevent fog, but some wind is essential, so that the air can be cooled rapidly.

During condensation fogs there is nearly always, at a few hundred feet above the ground, a layer where the air is warmer than the air below. On a nearly calm day this layer of warm air forms a ceiling below which fog forms. The formation of this layer is an important link between a smoke fog and a water fog.

METHODS FOR THE DETECTION OF TOXIC GASES IN INDUSTRY

CARBON BISULPHIDE VAPOUR

Erratum.—September issue, p. 675, l. 13, *for* "0·02" *read* "0·25 ml."

Straits Settlements

ANNUAL REPORT OF THE GOVERNMENT ANALYST'S DEPARTMENT FOR THE YEAR 1938

THE Report for 1938 by the Acting Government Analyst (Mr. A. C. Brooks) gives a detailed account of the work of the Laboratories of the Singapore and Penang Branches of the Department. In the Singapore Laboratory 20,647 samples and exhibits were examined for various Government departments, whilst in the Penang Laboratory the number was 5656.

CONTAMINATION OF LIQUOR BY LEAD.—Lead was determined in 382 samples of Chinese samsoo. In 27 the lead-content exceeded 0·75 p.p.m., and the importers were warned; ten samples contained more than 1·5 p.p.m., and importation of the consignment was prohibited. The heaviest contamination encountered was 7·1 p.p.m., and a sample from a consignment, distilled in Singapore and previously found to contain only a negligible trace of lead, contained 4·4 p.p.m. The contamination was traced to the glaze of the pots in which the liquor was shipped and stored. Fortunately it was found that the glaze yielded only a limited amount of lead, and that new jars can probably be rendered safe for use by washing out the soluble lead with dilute acid.

MATURITY OF BRANDY.—Legislation to extend to brandy the 3-years maturity requirement already in force for whiskey, was effected during the year. After January 1st, 1940, the importation of brandy will be prohibited unless it is officially certified to have been matured in wood for a period of not less than three years.

PERFUMES AND SPIRIT DUTIES.—In the Straits Settlements spirit duties are levied on Intoxicating Liquor and not on alcohol. This distinction exempts perfumes from payment of duty, provided that the alcohol used in their manufacture is sufficiently denatured with perfume oil to permit of its classification as "methylated spirits."

During the year the Customs Department submitted for classification 205 samples of perfume, mainly of local manufacture, prior to their release from bond. A quantitative estimation of the perfume oil in each sample was made, and 17 samples were classified as "not acceptable as perfume."

GHEE SUBSTITUTES.—There is a considerable local sale of imported refined and hardened vegetable and fish oils for use by the Mohammedan Indians as a substitute for ghee. In countries where such fats are used to replace lard they are sometimes known as "compound lard," and the use of this term on an invoice received in Penang caused a widespread rumour that these so-called vegetable oils were in fact derived from the pig, and there was much indignation among the users. Four samples of the fat were examined, but no evidence of the presence of fat of animal origin was found, and the importers and the public were reassured.

QUESTIONED DOCUMENTS.—An account book and a receipt book were submitted in a case in which the plaintiff alleged that an entry in the former had been made subsequent to the date stated, and that entries covering several months in the latter had been made within a few days of each other. No opinion could be expressed as to the relative ages of the entries, but it was found that the apparent newness of the account book entry was due to the use of a different kind of ink from that of the preceding and following entries, and that there had been at least three changes in the kind of ink used in the entries in the receipt book. In a case of alleged smuggling it was suggested that a pencil entry on one page of the ship's tally book had been made after the entry on the next page. A microscopical examination of the pencil impressions on both sides of the paper showed clearly that this was not possible.

POISONING CASES.—Of the 272 specimens of viscera, vomit, etc., examined, 181 were found to contain poison. The poisons detected included 78 of caustic soda, 16 of opium, 13 of tar oils, 13 of arsenic, 8 of tuba resin, 5 of cinnamon and clove oils, 4 of salicylic acid, 3 of formic acid, 2 of cyanide, 2 of mercury compounds, 2 of atropine, 2 of hydrochloric acid, and 1 each of various other deleterious substances.

In the Penang Laboratory 85 exhibits were examined and poisons were detected in 35. They included caustic soda or washing soda (17), arsenic (4), opium (3), alcohol (2), and one each of various other poisons.

A study of these results discloses, as in several previous years, the continued common use of caustic soda as a means of attempting suicide. To combat this, legislation has been introduced, making caustic soda a scheduled poison and thus rendering it more difficult to obtain. The most unusual case was that of a Chinese woman (a suicide) in whose alimentary tract was found not only morphine (probably taken as opium), but also 50 grams of coconut oil and copper sulphate equivalent to over 22 grams of the crystalline salt. The copper sulphate was probably administered as an emetic after the opium had been taken, and the coconut oil may have been intended as an antidote to one or both. After returning home the deceased tried to vomit, but failed, and shortly after became unconscious. The tongue and oesophagus were blackened, and the walls of the stomach and intestine were stained a vivid blue.

Face powders.—Four of six samples examined were satisfactory, but two contained much lead carbonate. Both of these came from a local factory, and one of them was directly associated with a case of lead poisoning.

BLOODSTAINS.—Blood was identified on 59 exhibits and demonstrated to be human in 51 of these. The blood on four exhibits—all connected with the same case—was found to be of a group other than that of the victim.

Blood from bugs.—In one case it was claimed by the defence that bloodstains on a garment were not connected with the alleged assault, but were produced by crushing bugs. The stains gave positive reactions for human blood, but experiments with bugs showed that, if these have battened on human beings, they yield

a fluid which gives positive reactions for human blood, if crushed within a period of about 24 hours. Similarly, dog ticks were found to give a fluid giving the reactions for dog's blood for about the same period after removal from the dog. Grouping was attempted on the stains referred to above, but the experiments were not successful.

COUNTERFEIT COINING.—Two cases, involving the examination of 27 exhibits, were investigated. In the first case the exhibits comprised a fairly complete outfit for the moulding of 5 cent, 10 cent and 20 cent counterfeits, the metal employed being a tin-lead alloy probably derived from empty chandu tubes. By the examination of the moulding flaws it was possible to identify with certainty the moulds in which many of the counterfeits had been made. In the other case the "coins" submitted were counterfeits composed of tin with a trace of copper. Evidence was given that two of the coins, from different exhibits, had been made in the same mould as each other.

FRAUDULENT QUACKERY.—Two Chinese, posing as qualified doctors, were charged with fraud, and their pharmaceutical stock-in-trade (41 exhibits) was examined. Victims of the hoax described a trick in which a blood-red colour appearing on the patient's skin proved his urgent need of treatment. It was demonstrated in Court how, by the use of certain of the exhibits, the trick could be performed. The presence of phosphorus and arsenic among the "medicines" led to additional charges under the Poisons Ordinance.

Alkali, Etc., Works

REPORT OF THE CHIEF INSPECTOR FOR THE YEAR 1938*

THE seventy-fifth Annual Report on the operation of the Alkali, Etc., Works Regulation Act, 1906, and the Alkali, Etc., Works Orders, 1928 and 1935, is by the Chief Inspector, Mr. W. A. Damon. It states that the number of works registered in 1938 was 980, involving 1857 processes. The totals, compared with those of 1937, show an increase of 22 processes in the same number of works. There have, in particular, been decreases in the number of sulphuric acid, chemical manure and sulphate of ammonia processes, whilst increased numbers of gas liquor, chlorine and benzene processes have been recorded. The number of visits paid during the year was 4385.

In connection with the inspections, 2185 analyses were made of the chimney gases escaping into the atmosphere. The average of all the total acidity tests was 1·05 grains per cb. ft., as compared with 1·06 grains in 1937.

FUME EMISSION.—A number of complaints, apart from those of smoke, relating to works not registrable under the Alkali Act have been investigated. The unpleasant odour resulting from the boiling of linseed oil has been considerably reduced, but not altogether removed, by a system of intensive washing with sprays. Further progress has been made in the de-dusting of blast furnace gas; this is essential if local nuisances are to be avoided. In a complaint of fumes from the combustion of crude coke oven gas it was found that the waste gases contained hydrogen sulphide. By the admission of more air and with a better system of control the nuisance has been abated.

Emission of lead fumes.—Several complaints that fumes of lead had caused injury to cattle and injurious deposits on vegetation were traced to a works where battery residues were melted. As soon as the matter was brought to the firm's notice the plant was shut down, and additional dust recovery plant was

* H.M. Stationery Office, York House, Kingway, London, W.C.2. 1939. Price 1/- net.

installed. It is proposed to make an Order extending the schedule of registered works by creating a new class designated "Lead Works."

SULPHURIC ACID WORKS.—The production of sulphuric acid in England and Wales in 1938 was 821,000 tons, calculated as monohydrate. This represents a decrease of 103,000 compared with the production in 1937. The low production has made it easy to operate, with an escape within the prescribed limit (4·0 grains as SO_3 per cb. ft.), and only six infractions have been noted. The average escape from contact plants tested was 3·30 grains, a figure very slightly less than last year, but yet high compared with that from chamber plants. Reasonably good conditions have been maintained in concentration plants, the average escape being 0·54 grain compared with 0·70 grain in 1937.

CHEMICAL MANURE WORKS.—The average escape of acid gas (0·057 grain per cb. ft., expressed as the SO_3 equivalent of hydrofluosilicic acid) from chemical manure works was substantially the same as the previous year. Where new scrubbing plant is contemplated it should be borne in mind that it is important that there should be early cooling and wetting of gases followed by adequate delay to allow time for the decomposition of the silicon tetrafluoride to be completed.

ALKALI AND COPPER (WET PROCESS) WORKS.—In 1938 the amount of salt decomposed in the salt cake process was 52,880 tons, and in the wet copper process 5160 tons. The average of tests to determine the escape of hydrochloric acid in this class of work showed 0·074 grain per cb. ft., as compared with 0·077 grain per cb. ft. in the previous year.

CEMENT PRODUCTION.—At the end of 1938 there were 121 rotary kilns in England and Wales with a combined capacity of 1158 tons of cement clinker per hour. There is satisfactory progress to record in the installation of dust arrestment plant. At the end of 1938 the proportion of the total capacity produced in kilns fitted with electrical precipitators was 47·2 per cent. With a suitable arrangement of chains a reduction of dust emission to about 0·5 grain per cb. ft. (at 15° C.) can be achieved. There is no reason why the erection of any new plant should be permitted unless guarantees can be given that the dust emission will be suitably dealt with.

AMMONIA PRODUCTS.—The total output of ammonia products in England and Wales was 677,200 tons expressed as sulphate (25·75 per cent. of NH_3). The production of concentrated liquor has continued to rise. Of 81 coke-oven installations in England and Wales, 35 practise indirect ammonia recovery. Many of the responsible officials at coke ovens where shock cooling (and recirculation) is employed admit that the practice does give rise to offence, and many attempts are being made to overcome the difficulty.

ACCIDENTS AT CHLORINE-USING PLANTS.—In a bleaching powder works an escape of chlorine was detected. It was found to be due to a broken distributor plate in one of the scrubbing towers. In another works chlorine is passed into a batch of caustic soda so as to be entirely absorbed, with the production of sodium hypochlorite. An accident occurred in these works owing to an obstruction in the valve, which resulted in an accelerated flow of gas such that some passed through the absorber. A man in the vicinity was slightly gassed, and instructions have now been given that an attendant must always be on the spot while the process is in operation.

VISCOSE WASTE GASES.—A series of tests has been made to determine the effect of chlorine on waste gases from the spinning of viscose, and a definite reduction in hydrogen sulphide has been found to result. The plan of dosing the gases with a small quantity of chlorine is used at many works; it is found to be a palliative, but by no means a complete cure. At one works the gases are being scrubbed with caustic soda, and at another the gases are drawn off from the machines and burned at the boilers. It has not yet been found possible, however, to burn the whole of the gases.

CARBON BISULPHIDE.—The conditions accompanying the manufacture of carbon bisulphide have improved, but the possibilities are by no means exhausted. The "dropping" of retorts into open barrows, with subsequent quenching, causes much fume, and an enclosed receptacle has recently been devised which should render the operation much less offensive. Redistillation of carbon bisulphide has also been the cause of offensive odour on many occasions when steaming has been unduly heavy and the seals have in consequence been blown.

REGISTERED PROCESSES IN SCOTLAND.—The number of works in Scotland registered under the Act was 92, in which 161 scheduled processes were operated. During the year, 216 visits of inspection were made and 105 chemical tests were carried out; 316 visits were also made to places not registered under the Act. Production in Scottish chemical industries decreased slightly, but remained on a satisfactory level. The diminution in output was most apparent in the coking industry. Tar distilled and sulphate of ammonia produced in coke-oven plants decreased by over 10 per cent.

Royal Sanitary Institute

ANNUAL CONGRESS

THE Annual Congress of the Royal Sanitary Institute was held at Scarborough from July 3rd to 7th. The Society was represented by Mr. Arnold R. Tankard, to whom we are indebted for the following notes on the proceedings.

The Inaugural Meeting was addressed by Lord Harewood, who, in an interesting Presidential Address, laid stress upon the importance of atmospheric pollution and its abatement.

At a meeting of the Sanitary Inspectors' session on Atmospheric Pollution there was an informative and valuable discussion. In the course of this, Mr. Tankard pointed out that most urban areas were more concerned with domestic than with industrial smoke, and that without some restrictive legislation it was much more difficult to remedy the former than the latter.

In the discussion on Clean Milk Production (Veterinary Hygiene session), Mr. Tankard put forward the view that the present bacteriological standards for graded milks were working well and were reasonable if somewhat lenient, but that more than half the milk supplies (liquid milk) were not subjected to any such standards or control, and that some criterion of bacterial purity should also be applied to these supplies, as they were largely consumed by the greater part of the population.

On the chemical side, Mr. Tankard directed attention to the fact that this Society had, through a specially appointed Committee, given special attention to dirty milk, and had devised a method for determining the amount of dirt in milk and for ascertaining its characteristics. He suggested that, as the Milk and Dairies Order required a standard of cleanliness, the standard for dirt in milk suggested by the Society should be given statutory authority.

British Standards Institution

THE following new British Standard Specification has been issued*:

NO. 868—1939. COD OIL FOR SULPHONATION PURPOSES.

This Specification is intended to include the technical provisions necessary for the supply of the product referred to, but does not purport to include all the necessary provisions of a contract. It does not apply to materials which are intended for medicinal use and are included in the British Pharmacopoeia.

DESCRIPTION.—Cod Oil for Sulphonation Purposes shall be the oil obtained mainly, if not entirely, from the liver of the cod, *Gadus morrhua* Linn. and other species of the family *Gadidae*. The oil may contain a small proportion of the oil obtained from the livers of other fish commonly caught in association with cod.

The oil shall be an orange to dark red liquid, and shall be free from foreign matter.

SPECIFIC GRAVITY AND DENSITY.—The sp.gr. at 15·5°/15·5° C. shall be not lower than 0·920 nor higher than 0·930. The density, or weight in air, at 15·5° C. of unit volume (1 ml.) shall be not lower than 0·918 nor higher than 0·928.

IODINE VALUE.—This shall be not lower than 145 nor higher than 178, when determined by the method specified (Wijs method).

SAPONIFICATION VALUE.—To be not lower than 180 nor higher than 190, when determined by the specified method.

ACIDITY.—The oil shall be free from mineral and added organic acids. The acidity, as determined by a method specified in an appendix, shall be agreed between Purchaser and Vendor.

UNSAPONIFIABLE MATTER.—The oil shall not contain more than 3 per cent. of unsaponifiable matter when determined by the specified method (Society of Public Analysts' method).

COLD TEST.—The congealing point, as determined by the following method, shall be agreed between Purchaser and Vendor:

Warm the oil to 30° C. and allow it to cool to 20° C. Fill a test-tube (18 mm. in diameter) to a height of about 30 mm. with the oil. Then draw out the tube and seal, or cork tightly, cut off the cork level with the top and coat suitably to exclude moisture.

Expose the tube containing the oil at 0° C. (or such other temperature as agreed between Purchaser and Vendor) for 24 hours. There shall be no deposit of stearine and the oil shall be fluid. The tube shall be kept in a vertical position during the test.

SAMPLING AND SIZE OF SAMPLE.—Representative samples, each measuring not less than 400 ml. (approx. ¾ pint) shall be, wherever possible, taken in triplicate from original containers or from the bulk, and shall be packed in clean, dry, air-tight, non-absorbent containers (preferably of glass). The containers shall be of such size that they are nearly filled by the sample. Each sample container so filled shall be marked with full details and date of sampling.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Separation of Sugars by the Chromatographic Adsorption of their Coloured Esters. I. Separation of Glucose and Fructose. W. S. Reich. (*Biochem. J.*, 1939, **33**, 1000–1004.)—When esterified with azobenzene-*p*-benzene-sulphonyl chloride or azobenzene-*p*-benzoyl chloride, sugars yield coloured esters that are readily separated by chromatographic adsorption. Brockmann alumina can be employed for this purpose, but the esters are eluted more completely from columns of silica (pure precip. B.D.H.). The separated ester yields the sugar itself on hydrolysis, and azobenzene-*p*-benzoyl esters are hydrolysed more easily than the sulphonyl esters, and are preferred for this reason. Azobenzene-*p*-benzoic acid is prepared by the condensation of *p*-aminobenzoic acid with nitrosobenzene in alcoholic acetic acid solution, and is converted into its acid chloride by treatment with thionyl chloride in benzene solution. Esterification of glucose or fructose,

* Publications Department, 28 Victoria Street, London, S.W.1. Price 2s.; post free 2s. 2d.

with formation of penta-azobenzene-*p*-benzoyl-glucose or -fructose, was effected by adding a mixture of the acid chloride and pyridine, cooled to −20° C., to the sugar, and allowing the mixture to stand for several days at 12° C. The excess of reagent was converted into the methyl ester by the addition of excess of methyl alcohol, and the precipitated sugar ester was filtered off and washed with ethyl alcohol. Equal weights of the glucose ester and fructose ester thus prepared were dissolved in chloroform, and the solution was diluted with 2 volumes of benzene and 2 volumes of petroleum spirit. The mixture was filtered through a column of silica (pure precip. B.D.H.) prepared from a suspension in a 1:3 mixture of benzene and petroleum spirit (b.p. 60–80° C.). After the addition of all the ester solution, the column consisted of two red zones separated by an orange zone. It was then developed by washing with a large volume of the mixture (1:3) of benzene and petroleum spirit. The dark orange zone that had thereby formed at the top of the column yielded almost pure fructose ester when eluted with a mixture of methyl alcohol and chloroform (1:4), whilst a second dark orange zone, separated from the first by a broad colourless zone containing one narrow orange ring, yielded almost pure glucose ester on elution. Thus a very satisfactory separation was obtained by one chromatographic adsorption. F. A. R.

Seed Fats of *Salvadora oleoides* and *Salvadora persica*. B. G. Gunde and T. P. Hilditch. (*J. Chem. Soc.*, 1939, 1015–1016.)—*Salvadora oleoides* and *Salvadora persica* (Indian names, jhal and pilu, respectively) *N.O. Salvadoraceae*, are small wild Indian shrubs with currant-like fruits and yellow seeds resembling those of mustard. The fruit-coats contained no fat but, on extraction with acetone, yielded about 1 per cent. of resinous material. The seeds constituted about 44 to 46 per cent. of the fruit, and the average weight of 100 seeds was 3·2 g. The seeds of (*a*) *Salvadora oleoides* and (*b*) *S. persica* yielded to petroleum spirit: (*a*) 41·0 and (*b*) 39·3 per cent., of pale yellow solid fats with the following characteristics:—saponification equiv., (*a*) 240·6, (*b*) 243·1; iodine value, (*a*) 5·5, (*b*) 6·1; acid value, (*a*) 1·0, (*b*) 2·2; unsaponifiable matter, (*a*) 0·7, (*b*) 0·8 per cent. The fatty acids had iodine value, (*a*) 5·0, (*b*) 5·5, and mean molecular weight, (*a*) 226·2, (*b*) 228·6. The mixed fatty acids of each fat were converted into methyl esters, which were fractionally distilled at 0·1 mm. through an electrically heated and packed column, and the fractions were analysed. Certain fractions were also examined quantitatively, and from the data obtained the composition (in per cent. mol.) of the acids was calculated to be:—decoic, (*a*) 2·0, (*b*) 1·3; lauric, (*a*) 24·1, (*b*) 22·3; myristic, (*a*) 52·7, (*b*) 54·6; palmitic, (*a*) 16·8, (*b*) 17·4; oleic, (*a*) 4·4, (*b*) 4·4. The data given differ considerably from those of Patel *et al.* (*J. Ind. Inst. Sci.*, 1926, 9a, 117). D. G. H.

Rice Bran as a Raw Material of Oil. T. Hidaka. (*J. Soc. Chem. Ind. Japan*, 1939, 42, 219–220B.)—The oils from fresh samples of rice bran taken throughout a year were extracted, and the free fatty acids were determined. The percentage rose steadily from 2·5 in the second month to 7·7 per cent. in the eleventh month. Rice brans from rice intended for food and from rice for saki, from both horizontal and vertical cleaning mills, were analysed. The two types of bran varied but little, but the horizontal mill produced a bran poor in starch

(average 13·95 per cent.) and rich in oil (20·38 per cent.), whilst the bran from the vertical mill was rich in starch (average 24·03 per cent.) and poor in oil (15·21 per cent.). Examination of samples of bran taken during cleaning operations showed that the free fatty acids in the oil decrease with the progress of cleaning, *e.g.* from 4·45 per cent. at the beginning to 1·42 at the end. Rice bran from a horizontal cleaning mill contained 11·0 per cent. of moisture and 20·0 per cent. of oil, and yielded 14 per cent. of oil and 80 per cent. of press-cake containing 8·0 per cent. of moisture and 8 per cent. of oil. The average percentage composition of the rice-bran cake on the market in 1938 was:—moisture, 8·0; oil, 8·7; starch, 18·0; protein, 15·8; ash, 11·0; P_2O_5, 4·1. D. G. H.

"Hibiscus Flowers" and its Principal Constituent. C. Griebel. (*Z. Unters. Lebensm.*, 1939, **77**, 561–571.)—A preparation sold under the name of "Jericho Rose," and more frequently as "Hibiscus Flowers," was identified botanically as the calyx of *Hibiscus sabdariffa* L. (Natural Order: *Malvaceae*), a plant indigeneous to tropical America and cultivated in many tropical regions for the agreeably acid taste imparted by the sepals to beverages, sauces, jellies and sweet foods. The drug consists of the dark purple-red sepals which, when dried, are brittle and may be reduced to a violet-red powder. The principal diagnostic microscopical features are the thick-walled, pitted, flattened, plate-like cells of the epidermis (which has a striated cuticle) and hypodermis, the large round, elongated almost tubular mucilage spaces in the mesophyll especially near the vascular bundles, the calcium oxalate crystals (reaching 35μ in length), which are very numerous near the veins, the isolated, frequently broken, bristly and sometimes curved or coiled hairs, and the spiral and reticulated vessels of the midrib partly surrounded by thickened bast fibres. The drug is characterised by its colour, its peculiar brittleness and its acid taste. The residue obtained by evaporation of the alcoholic extract of the drug was dissolved in water and treated with lead acetate solution. The granular precipitate of the lead salt was washed, suspended in water and decomposed with hydrogen sulphide, and, after removal of lead sulphide, the filtrate was evaporated to dryness. The residue was a viscous mass which, when dried for several days in a desiccator, formed a mass of radiating crystals. The filtrate from the separation of the lead salt was treated with basic lead acetate in the same manner, and a yellowish mass was obtained which could not be crystallised. A qualitative examination of these two fractions revealed the presence of some malic acid and a considerable amount of an acid which resembled citric acid in some of its reactions (*e.g.* with Denigès' reagent), but differed from it in several other respects and had some reactions in common with malic and tartaric acids. Its m.p. (181° to 183° C.) and the m.p. of its *p*-nitrobenzyl and phenacyl esters (172° C. and 177° C., respectively) and its optical rotation (+11°) also showed that it was not identical with any of these acids. Ultimate analysis of its lead salt and its phenacyl ester gave results corresponding with the empirical formula $C_6H_6O_7$, and the presence of two carboxyl groups was indicated. Analysis of the lead and quinine salts (which contain one molecule of water of crystallisation removed by drying at 105° C., but not at 100° C.) gave an equivalent weight of 95. The high oxygen:hydrogen ratio suggested a derivative of citric acid, and the

above-mentioned properties are consistent with the assumption that the compound is the lactone of hydroxycitric acid, which contains two asymmetric carbon atoms. This assumption is confirmed by the failure to form acid salts and by the fact that a solution of the compound made slightly alkaline to phenolphthalein becomes strongly acid again when warmed. The total titratable acid-content of the drug is 23 per cent., but this includes malic acid, another acid not yet investigated, and the red colouring matter which reacts with alkali. When the compound was isolated in the form of its lead salt, the yield was 13·6 per cent. When thin sections of the drug are immersed in hot lead acetate solution for an hour they turn bluish-green, and when mounted in chloral hydrate solution and examined microscopically are seen to be filled with needle-shaped crystals of the lead salt. The red anthocyanin colouring matter is extracted by 96 per cent. alcohol, and in aqueous solution gives greenish-blue and bluish grey-green precipitates with lead acetate and basic lead acetate solutions respectively. Mordanted wool fibre is not distinctly dyed. The sample contained about 8 per cent. of water and yielded 9·26 per cent. of ash containing much manganese. Per 100 g. of drug the aqueous extract (63·4 per cent.) yielded 7·6 g. of ash with alkalinity equivalent to 17·9 ml. $N/10$ Although titration of extracts with 2:6-dichlorophenol-indophenol indicated the presence of vitamin C, this could not be confirmed by other methods or by biological experiments, and this appears to be one of the rare instances in which this titration method leads to erroneous results. The drug appears to be a mild laxative and may be used for its agreeable thirst-quenching properties, but, apart from these, its therapeutic value is small, and the claims sometimes made for its action as a remedy in numerous illnesses are exaggerated and misleading. A. O. J.

Honeys Containing Octosan. W. Paul. (*Z. Unters. Lebensm.*, 1939, **78**, 30–36.)—Octosan is a mixture of highly-acetylated sugars, principally the acetic ester of sucrose, and, owing to its very bitter taste, it is used as a denaturant. It can be fed to bees with the usual bee-foods (*cf.* Wahl, *Z. Vergl. Physiol. Chem.*, 1936, **24**, 116), and in presence of moisture is gradually decomposed into acetic acid and sucrose, so that the bitter effect, which is due to the undecomposed octosan, disappears gradually. Octosan is detected in bee-food sugar by extracting 20 g. of the sample in a Soxhlet apparatus with 50 ml. of dry ether, than removing the solvent by evaporation, and dissolving the residue in 5 ml. of 96 per cent. alcohol at 40° to 50° C. To this solution are added 2 ml. of conc. sulphuric acid and 2 drops of a 15 per cent. solution of α-naphthol in alcohol, when an intense red-violet colour shows the presence of octosan (Molisch reaction). In the quantitative method 50 g. of sample are extracted with 100 ml. of dry ether, the extract is evaporated, and the residue is dissolved in 20 ml. of methyl alcohol. This solution is mixed with 20 ml. of 0·1 N potassium hydroxide solution, and allowed to stand for 30 minutes, after which the excess of alkali is titrated with 0·1 N hydrochloric acid; then 1 ml. of 0·1 N KOH consumed $\equiv$ 8·4 mg. of octosan. To a normal bee honey were added quantities of a solution of octosan in alcohol equivalent to 0·01 to 0·1 per cent. of octosan in the honey, and the taste was compared with that of untreated honey at intervals of two weeks at room-temperature. The bitter taste was no longer detectable after 6 and 14 weeks for the honeys containing

0·01 and 0·1 per cent. of octosan, respectively; the quantity of octosan normally used as a denaturant (0·075 per cent.) maintained its bitter effect for 12 weeks. There is reason to believe that the duration of the bitterness may vary according to the season of the year (see below). No appreciable influence on the sucrose-content of the honey, due to this treatment, could be detected. The detection of octosan in bee-honey is complicated by the fact that it undergoes progressive decomposition, forming sucrose, which may be already present in the honey, and acetic acid which, according to Nelson and Mottern (ANALYST, 1931, **56**, 403), also occurs naturally in honey. In the method suggested, however, 20 g. of honey are distilled with 30 g. of conc. phosphoric acid and 10 ml. of water in a 750-ml. round-bottomed flask, containing a little pumice and connected with a Liebig condenser, the end of the adaptor of which just touches the surface of 1 g. of dry calcium carbonate in a dish. Heating should be carried out cautiously to avoid foaming, and distillation is complete when no more liquid passes over and strong foaming starts in the flask. The contents of the dish are then dried at 120° C. and placed in an ignition tube, the outlet of which is directed on to a filter-paper that has been soaked in a fresh saturated solution of *o*-nitrobenzaldehyde in 2 *N* sodium hydroxide solution. When the powder is heated for 5 minutes at a low red heat, the calcium acetate present is decomposed into acetone, which produces a blue to blue-green colour on the yellow filter-paper (*cf.* Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, 2nd Ed., 1935, p. 408); addition of dilute hydrochloric acid to the paper destroys the yellow colour of the residual reagent, and leaves the blue of the indigo. This reaction gave negative results with 30 normal honeys and honeycombs of various types. A table shows the results obtained with 38 honeys from bees that had been fed on various diets, some containing octosans, for various periods and at various times of the year; these results are also correlated with the taste. Centrifuged honeys from bees that had been fed with sugar containing octosan in the autumn and pure sugar in the spring, gave little or no reaction for octosan and no bitter taste when examined in the following July or October. The use of an octosan sugar in both the autumn and spring resulted in a positive octosan reaction, although the honey was sweet. Honeycombs from bees that had been fed on octosan sugar in the winter, which were collected in March and tested in July, had a bitter taste and gave a positive octosan reaction. When an octosan sugar was used with the object of "over-feeding" the bee, so as to raise the yield of honey, the resulting honey had a positive octosan reaction.

J. G.

Standardisation of *Herba adonidis*. R. Koch. (*Deut. Apothztg.*, 1939, No. 33; *Pharm. Weekblad*, 1939, **76**, 1062–1063.)—The desirability of standardising the activity of this drug and preparations containing it is pointed out. It is used in place of *Digitalis*, especially in Russia, and in practice wide variations in activity have been observed corresponding with differences in the glucoside-contents. So far as is known, there are two *Adonis* glucosides: (i) adonivernoside, which is almost insoluble in water, readily soluble in chloroform or alcohol, sparingly soluble in ether, and insoluble in petroleum spirit; (ii) adonidoside, a yellow-white hygroscopic powder, which is readily soluble in water or alcohol, but insoluble in

chloroform, ether or petroleum spirit. Since only the former has stimulating and diuretic properties, it is apparent that the activity of a preparation will depend on the process used. Merck's adonidin is a mixture of *Adonis* glucosides of high activity, which is readily soluble in water and gives with hydrochloric acid the red-violet colour characteristic of the insoluble adonivernoside. If Merck's adonidin is taken as standard, *Herba adonidis* is found to have an activity corresponding with an average glucoside-content (according to Heyl, Hart and Schmidt) of approximately 1 per cent. J. G.

Alkaloids of *Mitragyne speciosa*. I. Mitragynine. H. R. Ing and C. G. Raison. (*J. Chem. Soc.*, 1939, 986–990.)—The dried leaves of *Mitragyne speciosa* (Kratom of the natives) obtained from Siam (*cf.* ANALYST, 1934, **59**, 753) were extracted with 70 per cent. alcohol. On evaporation the extract left an aqueous layer and a resinous solid, each yielding two picrates: one, mitragynine picrate (m.p. about 220° C.) and the other with m.p. 123–127° C. Choline alone was isolated from the mother liquor of the former. Mitragynine has been given the formula $C_{22}H_{30}O_4N_2$ (or possibly $C_{22}H_{32}O_4N_2$), but no crystalline derivative could be obtained from the second picrate, which appeared to contain one or more alkaloids isomeric with mitragynine. The four oxygen atoms of mitragynine are distributed as two methoxyl and one carbomethoxy groups. It is a mono-acidic base yielding a mono-methiodide and cannot be acetylated, so that the second nitrogen atom is regarded as non-basic indole nitrogen. No hydrogen is absorbed by the base in contact with platinum or palladium, and the only permanganate oxidation products that could be recognised were oxalic and acetic acids. On alkaline hydrolysis a relatively stable intermediate substance, $C_{22}H_{30}O_4N_2$, *R*OH, appears to be formed, which on further action of the alkali yields the acid $C_{21}H_{28}O_4N_2$. No crystalline product resulted from selenium dehydrogenation, and distillation with zinc dust gave a base $C_{14}H_{14}ON_2$, which is possibly an *N*-methyl-methoxyharmine, and unidentified substances which gave indole colour reactions. D. G. H.

Origin of the Objectionable Odour that occurs on Burning Unfermented Tobacco which has been Harvested while in a State of Vitality. A. Wenusch. (*Z. Unters. Lebensm.*, 1939, **78**, 46–48.)—It has been found that the rate of drying of tobacco is influenced by the method of harvesting used, and that in certain circumstances an unpleasant odour is produced when the tobacco smoulders. In particular, this occurs when the principal rib of the leaf is split during harvesting, as this lowers the state of vitality of the leaf and drying occurs comparatively rapidly. Leaves gathered in this way were dried, finely powdered, and extracted in succession in a Soxhlet apparatus with ether, absolute alcohol and water. A test for odour on burning was made after each extraction, and the same unpleasant odour resulted in each instance; its intensity was increased by the extraction with water. These experiments eliminate chlorophyll as the source of the odour, and suggest that protein matter is mainly responsible. The residue was then heated with hot dilute hydrochloric acid (1:5) for 12 hours, when only 30 per cent. of the original weight of tobacco remained; the odour,

however, was still apparent when the new residue was burned. Finally, this residue was treated with potassium hydroxide solution (1:20); only 7 per cent. of the tobacco then remained, and this was mainly cellulose, and when it burned the odour obtained was that of a burning cigarette paper and was free from the objectionable constituent. Confirmation that the odour is due to protein matter was obtained by digesting 5 g. of the powdered tobacco with 0·05 g. of trypsin for 24 hours at 30° C. in presence of 50 ml. of water and also of 4 per cent. ammonia. Comparison with control tests made with water and with the ammonia only, showed that the trypsin is necessary to remove the odour, and that it is particularly effective in presence of ammonia. It is considered that fermentation converts the proteins into a form in which they do not produce the undesirable odour when burned (*cf.* Wenusch, *id.*, 1937, **73**, 185; 1938, **76**, 41, 241, 433). J. G.

Biochemical

Colorimetric Method for the Estimation of Nicotinic Acid and Nicotinamide in Foodstuffs. H. Kringstad and T. Naess. (*Z. physiol. Chem.*, 1939, **260**, 108–118.)—Now that nicotinic acid (with its amide) has been established as the anti-pellagra factor, a method of estimating these substances chemically in foodstuffs is highly desirable, more especially as no satisfactory method of biological assay is at present available. There are two possible colorimetric methods—the first based on Vongerichte's dinitrochlorobenzene reaction, the second based on Koenig's reaction using cyanogen bromide and an aromatic amine. The second of these was selected for study, and the influence of various factors on the intensity of the colour produced was investigated. The optimum *p*H for both substances was found to be 6·1 to 6·5, but whereas the maximum colour was produced in 6 minutes with nicotinic acid, 23 minutes were required with the amide. The intensity of the colour also increased with increasing amounts of cyanogen bromide solution up to a maximum which was different for the two substances. Thus, when 0·35 ml. of the reagent was added to 10 ml. of a solution of the acid, two-thirds of the maximum colour developed, whereas a solution of the amide under similar conditions gave less than half this amount, thus making the difference between the acid and the amide more marked.

The material to be tested was minced and, after being thoroughly mixed with 2 to 3 times its volume of water, was heated for 1 hour on the steam-bath and filtered. The residue was extracted twice more, and the combined extracts were treated with sulphuric acid until the acidity was equivalent to 0·1 *N*. The liquid was then heated for 2 hours at 100° C. to liberate nicotinamide from the co-enzyme and the sulphuric acid was neutralised by addition of baryta and the barium sulphate filtered off. The filtrate was diluted to a suitable volume, and 20 ml. were made up to 25 ml. with phosphate buffer solution (17·60 g. of potassium dihydrogen phosphate and 6·67 g. of disodium phosphate were dissolved in water and the solution made up to 250 ml.), giving a *p*H of 6·3. Ten ml. of this solution, containing 1 to 50γ of nicotinamide, were transferred to the cell of a Pulfrich photometer and 4 drops of aniline solution (presumably saturated) followed by 0·35 ml.

of cyanogen bromide solution* were added. The other cell contained nicotinamide solution without added reagents. Filter S.47 (and later S.45) was used, the maximum colour developed was measured and the amount of nicotinamide present was calculated by reference to a standard curve. Another portion of the extract (100 ml.) was heated on the steam-bath with 15 g. of (hydrated) barium hydroxide for 2 hours, to hydrolyse the amide quantitatively to nicotinic acid. The solution was neutralised with sulphuric acid and centrifuged. The barium sulphate precipitate was washed with three 25-ml. portions of hot water, and the combined filtrate and washings were made up to volume. The measurement of the colour was carried out as for nicotinamide. Almost quantitative recovery of added nicotinic acid and nicotinamide was obtained by the method. The following are the most important results obtained for the nicotinic acid and amide contents of foodstuffs:

	Estimated as nicotinamide mg. per 100 g.	Estimated as nicotinic acid mg. per 100 g.
Beef	4·9	4·9
Pork	—	3·3
Ox-liver	15·5 to 18·7	15·5 to 20·0
Cod (muscle, roe or liver)	1·4 to 1·6	1·4 to 1·7
Salmon (preserved)	6·4	6·0
Herring	2·1	2·9
Potato	0·5	1·0
Wheat-bran	—	5·0
Rye	—	1·3
Wheat-germ	—	4·2
Maize	1·7	1·3
Brewers' yeast (dried)	—	45·5

These values agree well with such biological results as have so far been obtained.

F. A. R.

Estimation of Nicotine in Urine. A. C. Corcoran, O. M. Helmer and I. H. Page. (*J. Biol. Chem.*, 1939, **129**, 89–97.)—Two methods for the estimation of nicotine in urine were investigated. The first, depending on the formation of a precipitate of nicotine reineckate and measurement of the colour of its solution in diacetone, was found to be applicable to amounts of nicotine greater than 2·0 mg. The second, depending on Koenig's reaction with cyanogen bromide and a base, was found to be capable of detecting 0·05 mg. of nicotine.

Method 1.—A 24-hour urine sample preserved with chloroform is made alkaline with 5 ml. of 40 per cent. sodium hydroxide solution and extracted with ether in a continuous extractor for 36 to 48 hours, 15 ml. of 0·1 *N* hydrochloric acid being placed in the receiver. At the end of the extraction the ether is distilled from the extract, the residual aqueous solution is transferred to a 500-ml. Erlenmeyer flask, and the *p*H is adjusted to 3·0. The original receiver is rinsed with two or three 10-ml. portions of Sørensen's 0·15 *M* citrate buffer solution, *p*H 3·0, and the rinsings are poured into the Erlenmeyer flask. The solution is then steam-distilled for 50 to 60 minutes and the distillate is discarded, thus removing

* Concentration not stated; presumably 4 to 5 per cent.—F.A.R.

pyridine and homologues. After cooling, the solution is made alkaline to phenolphthalein and again steam-distilled for 50 to 60 minutes into a flask containing 15 ml. of 0·1 *N* hydrochloric acid, an adaptor dipping well below the surface of the acid being used. The acid is concentrated under reduced pressure to 3 to 5 ml., transferred to a 50-ml. beaker, and followed by four 5-ml. rinsings of water. The solution is evaporated on the steam-bath to about 1 ml. and transferred to a 15-ml. graduated centrifuge tube with the aid of three 1-ml. portions of water. The solution is made up to 5 ml. with water, 10 ml. of a freshly prepared, cold, saturated solution of Reinecke salt are added, the liquids are mixed, and the tube is allowed to stand at 2° to 3° C. for 3 hours. The precipitate is filtered off with the aid of a Pregl filter-tube, and washed with several 1-ml. portions of cold water until the washings are colourless. The filter-tube is then washed into a 10- or 25-ml. graduated flask with several 1-ml. portions of diacetone until all the reineckate has been extracted, after which the solution is made up to volume. Its colour is measured by means of a photoelectric colorimeter (filter No. 520), pure diacetone being used in the compensating tube. The nicotine-content is calculated from a calibration curve. The recovery of nicotine, added to 250-ml. portions of distilled water (no ether extraction or steam-distillation), was 100 per cent. The recovery of 2·0 mg. of nicotine, added to non-smoker's urine, was 85 to 92 per cent., but the colour equivalent of non-smoker's urine was 0·3 mg. per 24 hours.

Method 2.—A portion of urine containing about 0·2 mg. of nicotine is made alkaline to phenolphthalein with 40 per cent. sodium hydroxide solution and concentrated by distillation to a volume of 5 to 10 ml., the distillate being collected in, and below the surface of, 20 ml. of *N* hydrochloric acid. The distillate is concentrated on the steam-bath to 5 to 10 ml. and made alkaline to phenol red with *N* sodium hydroxide solution. The solution is then extracted with three 40-ml. portions of ether, and the combined ethereal extracts are distilled after addition of 5 ml. of *N* hydrochloric acid. To the residue so obtained 8 drops of 0·02 per cent. *o*-cresolphthalein solution are added, and the reaction of the solution is adjusted with 0·1 *N* sodium hydroxide solution and hydrochloric acid until the colour has just disappeared (approximately *p*H 8·2). The solution is transferred to a 25-ml. flask and made up to volume with 12 per cent. sodium acetate solution and water, so that the final solution contains 3 per cent. of sodium acetate. Five ml. of this solution are transferred to a colorimeter tube, and 2 ml. of cyanogen bromide solution are added. (This is prepared by dissolving 4 g. of sodium bromide, 3 g. of sodium bromate and 3 g. of sodium cyanide in 90 ml. of water, cooling the solution to 0° C. and slowly adding 10 ml. of 12 *N* sulphuric acid.) After being cooled in an ice-bath for 45 minutes the solution is treated dropwise with 4 ml. of alcoholic benzidine solution (50 mg. per 100 ml.), and the colour is measured 7 to 13 minutes afterwards at half-minute intervals, 3 per cent. sodium acetate solution being used in the compensating tube with filter No. 420. The nicotine-content is calculated from the maximum extinction observed by reference to a calibration curve. Recoveries of 87 to 100 per cent. of nicotine added in amounts of 0·20 to 0·40 mg. were obtained. The second method is the more convenient and accurate. F. A. R.

Determination of Chlorides in Biological Fluids by the Use of Adsorption Indicators. A. Saifer and J. Hughes. (*J. Biol. Chem.*, 1939, **129**, 273–281.)—To 0·2 ml. of urine in a Pyrex test-tube were added 3 drops of 3 per cent. hydrogen peroxide (chloride-free), and the tube was heated in a boiling water-bath for 2 minutes. Five ml. of 0·45 per cent. (hydrated) zinc sulphate solution and 1·0 ml. of 0·1 *N* sodium hydroxide solution were added, and the tube was heated in the water-bath for a further 3 minutes. After cooling, the contents were filtered (or centrifuged), and the filtrate and washings were transferred to a 25-ml. conical flask. Two drops of dichlorofluorescein indicator (0·05 per cent. solution in 50 per cent. alcohol) were added, and the solution was titrated with 0·02 *N* silver nitrate solution to the first definite pink colour that appeared throughout the solution. The results obtained by this method agreed very closely with results obtained by Caldwell and Moyer's modification (*Ind. Eng. Chem. Anal. Ed.*, 1935, **7**, 38) of the Volhard method and by Van Slyke's nitric acid digestion method (*J. Biol. Chem.*, 1923–24, **58**, 523). Albuminous urines also gave results in agreement with those obtained by the Van Slyke method. With the latter as standard, the maximum error was about 2 per cent., and the average less than 1 per cent.

Chloride determinations were also made by this method on zinc filtrates of blood serum or plasma. The latter (0·2 ml.) was pipetted into a Pyrex test-tube, and 1·0 ml. of 0·1 *N* sodium hydroxide solution was added, followed by 5·0 ml. of 0·45 per cent. zinc sulphate solution, drop by drop. The liquid was then heated in a boiling water-bath for 3 minutes, cooled, filtered, and titrated as described above. Whole blood zinc filtrates were similarly titrated. The average deviation of the method was ± 2 per cent. F. A. R.

Micro-estimation of Fluorine in Blood. H. Wulle. (*Z. physiol. Chem.*, 1939, **260**, 169–174.)—The method proposed by Kraft (*Z. physiol. Chem.*, 1937, **246**, 233) has been modified. The first stage, namely, the ashing of the blood serum, was found to be subject to a grave risk of error through loss of fluorine, and to avoid this, the following procedure was adopted. The serum was charred in a porcelain crucible, and the residue transferred to a gold crucible and finely powdered. A carefully regulated stream of oxygen was passed into the crucible, which was meanwhile gently ignited. Sintering of the ash, which should be quite colourless after an hour's heating, must be avoided. This method of ashing was found to be superior to ignition either with sodium peroxide or with potassium perchlorate. The second stage comprised the distillation of the ash with powdered glass (not siliceous earth, which adsorbs fluorine) and sulphuric acid at 135° to 140° C. in a current of steam, the fluosilicic acid that distilled being collected in sodium hydroxide solution. When more than 20γ of fluorine were present, distillation was incomplete, and it is recommended that three successive distillations should be carried out. The third and final stage consisted in the titration of the fluoride solution with the acid zirconium oxychloride-purpurin reagent of Kolthoff (*Ind. Eng. Chem. Anal. Ed.*, 1934, **6**, 118). It was found advantageous to dilute the purpurin solutions, as used by Kolthoff, with an equal volume of water and to make the fluoride solution neutral before titrating. Horse-blood serum was found to contain 80 to 90γ of fluorine per 100 ml. and human serum (70 analyses) from 35 to 145γ per 100 ml. F. A. R.

Occurrence of Free Vitamin A Alcohol in Fish Livers.—T. H. Mead. (*Pharm. J.*, 1939, **143**, 102–103.)—Fresh livers from the ling (*Molva molva, M. vulgaris* Day) were stored in solid carbon dioxide before the oil was extracted. The minced livers were then ground with sand and anhydrous sodium sulphate and extracted with cold peroxide-free ether. The ether was removed by distillation in nitrogen, and the oil was immediately heated for a short time at 100° C. in a high vacuum to remove traces of water and inactivate any hydrolytic enzymes. Two batches of such oil were subjected to molecular distillation, the apparatus and technique of Hickman being used. Of the total vitamin A present, 1·9 and 1·8 per cent., respectively, distilled at, or below, 150° C.; after allowance had been made for the overlapping of the elimination curves of vitamin A alcohol and vitamin A esters, it was concluded that not more than 1·0 per cent. of vitamin A alcohol was present in the first batch of oil and not more than 2·1 per cent. in the second batch. F. A. R.

Determination of Anti-neuritic Vitamin in Natural Materials. P. Meunier and C. Blancpain. (*Compt. rend.*, 1939, **208**, 768–770.)—The method depends on measurement of the colour developed by the reaction of the substance with diazotised sulphanilic acid alone and in presence of potassium ferricyanide. Vitamin B_1 gives a coloured product only in the absence of potassium ferricyanide, whilst other amino compounds which may accompany the vitamin, such as histidine, histamine, thiazol, and tyrosine, give colours which are not affected by the ferricyanide, enabling the vitamin to be determined by difference. Meunier's electrophotometric technique is employed (*Bull. Soc. Chim. Biol.*, 1937, **19**, 113). Into the photometric cell are introduced 2 drops of a 1 per cent. solution of sulphanilic acid in 10 per cent. hydrochloric acid and 4 ml. of Kinnersley and Peters' solution ($N/2$ sodium hydroxide solution containing 2·9 per cent. of sodium bicarbonate) to which has been added 0·3 per cent. of sodium nitrite. After a few seconds 1 ml. of the solution to be tested (pH 5 to 6 and containing 3 to 30γ of vitamin B_1) are added. Photometric readings are made (with the use of the green light-filter) exactly 30 seconds after the addition, and at 15-second intervals for a further minute. The process is repeated with a similar quantity of the solution to be tested to which has been added 0·1 per cent. of potassium ferricyanide. The photometric reading-time curve is plotted for both sets of readings: the difference between the readings (ordinates) gives a measure of the vitamin content. Tests were carried out with yeast extract. S. G. C.

Vitamin K from Alfalfa. P. Karrer and A. Geiger. (*Helv. Chim. Acta*, 1939, **22**, 945–948.)—Pure vitamin K_1 obtained from alfalfa is an oil, for which the name α-phylloquinone is proposed. Analysis and molecular-weight determination indicate a formula between $C_{30}H_{44-46}O_2$ and $C_{32}H_{48-50}O_2$. It is unstable to light, and possesses quinonoid properties, being reduced by zinc and acetic acid or by sodium hydrosulphite to a colourless hydroquinone that is readily re-oxidised by atmospheric oxygen to the original quinone. The vitamin can, in fact, be reduced potentiometrically with sodium hydrosulphite solution in 80 per cent. alcohol buffered with sodium acetate (0·02 N) and acetic acid (0·02 N). The titration is carried out at 25° C., and the titration-curve has a well-defined

plateau corresponding with a molecular weight of 446. The redox potential is equal to +0·005 volt. In acetic acid solution, α-phylloquinone can be catalytically reduced, four molecules of hydrogen being taken up. By a reducing acetylation, a colourless hydroquinone acetate with an absorption maximum at 282$m\mu$ and a minimum at 250$m\mu$, is formed. F. A. R.

Colour Reactions in Vitamin K Concentrates. H. J. Almquist and A. A. Klose. (*J. Amer. Chem. Soc.*, 1939, **61**, 1610–1611.)—The colour reaction first described by Dam, Karrer *et al.* (*Helv. Chim. Acta*, 1939, **22**, 310) affords an easy method of assessing the vitamin K activity of concentrates. A few mg. of the concentrate are dissolved in 1 to 2 ml. of methyl alcohol, and 1 ml. of sodium methylate solution (2 to 3 g. of sodium dissolved in 50 ml. of methyl alcohol) is added. When warmed for a few minutes, the mixture slowly develops a distinct purple colour if sufficient vitamin K is present and interfering pigments are absent. Soon the colour changes to a reddish-purple and finally to a reddish-brown. Carotenoid pigments can be extracted from the solution at this stage by means of petroleum spirit, leaving the reaction product in the methyl alcohol layer. The colour intensity of this solution showed a close correlation with the biological activity of the original concentrate. F. A. R.

Derivatives of Vitamins K_1 and K_2. S. B. Binkley, D. W. MacCorquodale, L. C. Cheney, S. A. Thayer, R. W. McKee, and E. A. Doisy. (*J. Amer. Chem. Soc.*, 1939, **61**, 1612–1613.)—Reductive acetylation of vitamin K_1 (from alfalfa) resulted in the formation of the diacetate of dihydro-vitamin K_1, which crystallised readily from petroleum spirit (b.p. 30° to 60° C.), or methyl alcohol, in fine white needles, m.p. 59° C. Analysis agreed with the composition $C_{36}H_{56}O_4$. The substance possessed marked vitamin K activity, and its absorption spectrum showed intense absorption at 230 $m\mu$, where $E^{1\%}_{1\,cm.}$ was 1250. The compound was not readily hydrolysed, but was converted into vitamin K_1 by treatment with methyl magnesium iodide, followed by shaking an ethereal solution of the product with air. The vitamin had the composition $C_{32}H_{48}O_2$. In a similar way vitamin K_2 (from putrefied fish meal) was converted into the diacetate of dihydro-vitamin K_2. This had m.p. 57° to 58° C. and the composition $C_{44}H_{60-62}O_4$. It also was biologically active and had an absorption spectrum very similar to that of the vitamin K_1 derivative. F. A. R.

Colour Reaction for Vitamin K. E. Fernholz, S. Ansbacher and M. L. Moore. (*J. Amer. Chem. Soc.*, 1939, **61**, 1613–1614.)—The colour reaction described by Dam *et al.* (*Helv. Chim. Acta*, 1939, **22**, 310), and claimed by them to be characteristic of vitamin K is not a criterion for the presence of the vitamin. A concentrate having high biological activity and giving the colour reaction very strongly was chromatographed on a column of heat-activated calcium sulphate from petroleum spirit solution. The fraction eluted from the column gave an intense colour reaction, but was biologically inactive, whereas the filtrate gave only a slight darkening with the ethylate solution and contained all the biological activity of the original preparation. By repeated chromatographic adsorption, an apparently homogeneous substance was obtained, comparable in biological

activity with the vitamin K_1 of McKee *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 1295). During the last stages of the isolation process, the sodium ethylate colour reaction became positive, but never reached the intensity of the inactive fraction previously separated. It is believed that the blue colour is due to readily formed decomposition products of vitamin K. F. A. R.

Organic

Separation of Mixtures of Dicarboxylic Acids. F. Rennkamp. (*Z. physiol. Chem.*, 1939, **260**, 276–278.)—Although the higher dicarboxylic acids, unlike the corresponding fatty acids, can generally be separated from one another by fractional crystallisation, the increasing importance of such acids in biological work makes it desirable to find a method of separation that can be used when a variety of other compounds are present in addition. A study was therefore made of the separation by distillation of the methyl esters of azelaic and sebacic acids. A mixture of known weights of the two acids was esterified with methyl alcohol and sulphuric acid, and the mixed ester (obtained in 97·6 per cent. yield) was distilled at 125° to 140° C. under a vacuum of 0·01 to 0·02 mm. Of the eleven fractions collected, the first two yielded pure azelaic acid on hydrolysis, and the last four yielded pure sebacic acid. The azelaic acid contents of the intermediate fractions (after hydrolysis) were calculated from their equivalent weights determined by titration with standard alkali. The total azelaic acid thus found was 38·24 per cent., as compared with 36·71 per cent. actually present. F. A. R.

Colorimetric Reaction for the Detection and Determination of Small Quantities of β-Naphthol. J. A. Gautier. (*J. Pharm. Chim.*, 1939, **30**, 70–76.)—Very small quantities of β-naphthol, of the order of 1 mg. or less, can be detected and determined by means of the pink or red colour produced when β-naphthol reacts with nitrous acid. The reaction is not given by α-naphthol or β-naphthyl ethers.

Detection of β-Naphthol.—When 1 ml. of a solution of β-naphthol in 30 per cent. alcohol, the concentration of the solution being between $M/20$ (0·72 g. in 100 ml.) and $M/1000$ (0·0144 g. in 100 ml.) is treated with 1 drop to 2 ml. (according to the presumed concentration of the β-naphthol) of $N/10$ sodium nitrite solution (0·69 g. in 100 ml.) and a volume of N hydrochloric acid equal to that of the nitrite solution, and the volume of the liquid is made up to 10 ml. with water, there develops a pink to red colour. The time required for the formation of the colour decreases from a few minutes to a few seconds with increasing quantities of the naphthol, and at the same time the stability of the colour decreases from several hours to about 15 minutes. The sensitivity of the reaction can be increased still further by diluting to less than 10 ml.

A drop reaction can be carried out by mixing on a porcelain plate 1 drop of the β-naphthol solution, 1 drop of the nitrite solution, and 1 drop of the acid. Under these conditions an $M/10{,}000$ β-naphthol solution gives a pink colour in about 10 minutes.

Colorimetric Determination.—A scale of colours is formed by diluting to 10 ml.

volumes of the naphthol solution ranging from 0·10 to 5 ml. and treating the solution with volumes of the nitrite solution and acid equal to half the volume of the naphthol solution (with a minimum of 2 drops of the acid). The colour of the test solution may be compared with these standards by dilution or in a colorimeter. Because of the difficulty of comparing deep red colours in the colorimeter it is of advantage to use a continuous scale of colours including that of the supposed concentration of the naphthol solution. The standard colours should be prepared at the same time as that of the solution under test. E. M. P.

Analysis of Natural Perfumes by Entrainment at Low Pressure with Ethylene Glycol. S. Sabetay. (*Ann. Chim. anal.*, 1939, **21**, 173–176.)—Simple and rapid methods for the analysis of natural perfumes are dependent on a distillation process, and distillation in superheated steam has been found satisfactory for control work by Naves, Sabetay and Palfray (*id.*, 1937, **19**, 201). A simpler method is based on the fact (use of which is made in industrial operations) that in a vacuum the volatile fractions of most natural perfumes are entrained by the vapour of ethylene glycol. From 1 to 10 g. of the sample are treated in a 50 to 75-ml. Vigreux vacuum distillation-flask with 20 ml. of ethylene glycol, and distillation is carried out at 8 to 15 mm. pressure and 90° to 100° C. in an oil-bath, which is maintained at 125° to 145° C. The residue is then usually odourless, but as a precaution a second distillation is carried out with a further 20 ml. of ethylene glycol, the distillate being collected separately. Exceptionally a third similar distillation may be necessary, and an indication of whether it is required is obtained on adding 100 and 50 ml. of water to the first and second distillates, respectively; if no appreciable quantity of oil separates from the latter, the third distillation is unnecessary. The diluted distillates are then saturated with salt (about 30 g.) and extracted in succession with three 20-ml. portions of a mixture in equal volumes of pentane and ether; this mixture dissolves only negligible quantities of the ethylene glycol, and for this reason is preferable to ether alone. A fourth or fifth extraction may be required in exceptional cases. The solvent mixture is dried by means of anhydrous sodium sulphate and filtered, and the filter is washed with some of the solvent. The filtrate is then evaporated in a tared flask at 15 to 20 mm. pressure, until there is no further loss in weight, and the weighed residue, which consists of the true perfume, is subjected to olfactory examination, and its physico-chemical constants are determined. The method gives results which agree satisfactorily with those obtained by the method of Naves, Sabetay and Palfray (*loc. cit.*). Since ethyl phthalate is also carried over to a great extent by the ethylene glycol, tests for the former in the distillate (*cf.* Naves and Sabetay, ANALYST, 1938, **63**, 208) will reveal adulteration of this nature. Below are summarised (*a*) the yields (percentages), (*b*) the n_D^{20} of the volatile fractions separated from a number of perfumes in this way, and (*c*) the number of distillations necessary, respectively:—Jasmine, (*a*) 15, (*b*) 1·5001, (*c*) 1; jasmine (absolute), (*a*) 30·70, (*b*) 1·4963, (*c*) 2; rose, (*a*) 30·50, (*b*) 1·5055, (*c*) 1; rose (absolute), (*a*) 51·1, (*b*) 1·5116, (*c*) 1; orange (absolute), (*a*) 42, (*b*) 1·4883, (*c*) 1; violet (absolute), (*a*) 7·10 (nonadienal, 42·8 per cent.), (*b*) 1·4834, (*c*) 1; polyanthus (absolute), (*a*) 14·5, (*b*) 1·5319, (*c*) 1; lavender (absolute), (*a*) 73·6, (*b*) 1·4690, (*c*) 1; *Boronia megastigma*,

(*a*) 19·4 (β-ionone, 41·5 per cent.), (*b*) 1·4786, (*c*) 2; immortelle, (*a*) 4·9, (*b*) 1·5032, (*c*) 2; geranium (absolute), (*a*) 84·2, (*b*) 1·4771, (*c*) 1; musk, (*a*) 7·6, (*b*) 1·4923, (*c*) 1; Mousse de Chêne, (*a*) 7·3, —, (*c*) 2; civet, (*a*) 9·3, —, (*c*) 2. J. G.

Improved Method for the Determination of the Acidity and *p*H of Paper. H. F. Launer. (*J. Res. Nat. Bur. Stand.*, 1939, **22**, 553–564; *Chemical Age*, 1939, **41**, 25.)—At present it is usual to prepare an extract of paper for determinations of *p*H and acidity by extracting 5 g. with 250 ml. of distilled water under a reflux condenser for 1 hour in a water-bath at 95° to 100° C. (but not boiling). This method has been criticised (*cf.* Grant, *Proc. Tech. Sect. Paper Makers' Assoc.*, 1939, **19**; in the press), and the author has now found that the *p*H values of such extracts are very susceptible to variations in the duration and temperature of the extraction, and that the same *p*H values are obtained by the following method, which, however, is less affected by such influences:—The paper (1 g., air-dry) is macerated with 20 ml. of distilled water until wet, 50 ml. of water are added, and the mixture is allowed to stand at 20° to 30° C. for at least 30 minutes (preferably for 1 hour). The *p*H of the extract can then be determined without removing the paper, thus avoiding errors due to filtration and to incidental contamination by the atmosphere inherent in the present method. Thick kraft papers should first be ground, presumably in a mill of the Koerner type (see Burton and Rasch, *J. Res. Nat. Bur. Stand.*, 1931, **6**, 605), which is used at present and which enables the paper to be disintegrated without contamination or overheating; with such papers the period of extraction should be 20 hours. The standard procedure specified by the A.S.T.M. for the purification of the water used is considered unnecessarily severe, as the *p*H of the water need not be exactly 7, the same results being obtained with waters of *p*H 6·7 and 5·9. The *p*H values obtained by the method now described correspond satisfactorily with the amounts of alum used, and are equivalent to hydrogen ion concentrations of about 25 per cent. of those obtained by the standard method. J. G.

Examination of Writing made with Aniline Dyes. F. Künkele. (*Z. Unters. Lebensm.*, 1939, **77**, 596–602.)—In the chemical and physical examination of ink marks much less depends upon the identification of the dye than upon clearly establishing distinct differences between one mark and another. Similarities are of value only when the ink contains unusual constituents. In a preliminary examination with the naked eye differences are often apparent, but small differences in colour should be interpreted with caution, since they are often due to differences in the rate of movement of the pen, and still more often to the age of the document, the cleanliness of the ink, the kind of paper and the preservative constituent of the ink. On the other hand, especially with the rarer dyes, colours similar in appearance may be chemically different. The microscopical examination of marks made with aniline inks rarely gives useful results unless one of the inks contained deposits caused by dirt, dust or admixture with other ink. Many inks give a characteristic fluorescence in ultra-violet light. The test is useful, but mere colour differences which are not recognisable as distinct fluorescence should be disregarded. Occasionally, more definite results are obtained if the mark is first moistened with water and alcohol and dried. The reagents recommended for

the examination of modern aniline inks are water, alcohol (96 per cent.), conc. sulphuric acid and 10 per cent. solutions of hydrochloric acid, ammonia and potassium hydroxide. A mark is lightly rubbed with a small cotton-wool pad charged with alcohol which dissolves the dye and gives a true indication of its colour. Another mark is treated with a drop of conc. sulphuric acid, which gives an immediate reaction with many dyes. After 30 seconds two drops of water are added and mixing is effected by blowing through a capillary tube (9 to 10 cm. long and 1 mm. internal diameter) held 1 to 2 cm. above the surface of the drop. In many instances a distinct colour change follows the addition of water. Other marks are treated with drops of 10 per cent. hydrochloric acid, 10 per cent. ammonia and 10 per cent. potassium hydroxide solutions. The last two reagents do not give characteristic reactions with many dyes. The reactions should be observed within 30 seconds, after which the drops are drawn up on filter-paper and, if necessary for the safety of the document, the places treated may be neutralised with ammonia or dilute acetic acid. It is often advisable to place a drop of water on the mark and transfer the solution of the dye by means of a capillary tube to a porcelain plate on which the drop is allowed to dry before being subjected to the tests. When the document has no special value, the stained fibres may be removed by gentle scraping and examined through binocular lenses in an appropriate light. Black inks, which are often mixtures of dyes, are not easily differentiated. The following procedure is frequently applicable. A strongly tinted mark is moistened with a little water and lightly rubbed, and the solution is transferred to a porcelain plate and concentrated by gentle evaporation. The surface of the drop is touched uniformly with the end of a strip of filter-paper, 1 mm. broad, held vertically. Red and green dyes rise more rapidly and to greater heights than the blue constituents, so that a separation is effected. Individual blue ink markings are often differentiated by exact observation of the chemical tests, especially those with hydrochloric acid and ammonia and particularly with marks of equal colour intensity on the same document. In many instances Feigl's method of distinguishing acidic and basic dyes (*Qualitative Analyse mit Hilfe der Tüpfelreaktionen*, Leipzig, 1938, p. 498) is useful. Sufficient stearic acid and urea to form layers 0·5 cm. deep are melted in a test-tube. Cuttings or scrapings from the document are placed in the mixture, which is then warmed for a short time. Acidic dyes colour the lower urea layer and basic dyes the upper stearic acid layer. Modern iron-gall inks contain an aniline dye which provides the colour before the latent iron tannate colour forms on the paper. When treated with a drop of water the aniline dye usually dissolves before the iron tannate, especially if the document is old, and the dye may thus be separated for testing. An exhaustive list of the aniline dyes used in ink manufacture cannot be given. According to Becher (*Die Fabrikation der Tinten, Tuschen und Stempelfarben*, Augsburg, 1936), the following are some of the dyes commonly used:—Acidic dyes: nigrosin, Agalma-black TG, brilliant black BX, naphthylamine black S, naphthol blue-black, "artificial silk black" 3G, Neptune blue R, cyanol extra, water blue I, alkali blue 7, light green SF, green PLX, Neptune green SGO and SBX, alkali fast green 3G, Havanna brown G, Neptune brown RX, eosin A salt-free T, acid fuchsin O, brilliant crocein MOOL, ponceau RR, sorbic red X, orange II,

orange GG, tartrazin XX, fast yellow Y, quinoline yellow KT, metanil yellow extra. Basic dyes: methylene blue, marine blue, Victoria blue B, Victoria pure blue BO, methyl violet, crystal violet, ethyl violet, diamond green BXX (malachite green), fuchsin A, rhodamine B extra, safranine T, chrysoidine RL, euchrysine.

A. O. J.

Inorganic

Determination of Zinc and Copper with Morpholine. L. S. Malowan. (*Mikrochem.*, 1939, **26**, 319–321.)—Morpholine ($O:(CH_2CH_2)_2:NH$), a cyclic amine which is miscible with water in all proportions, yields precipitates, insoluble in excess of the reagent, with a number of metals, including zinc and copper, which form soluble complex salts with excess of ammonia. The precipitates are crystalline and easy to filter. The reagent may be used for the determination of zinc and of copper from pure solutions, with results as accurate as those obtained by the sodium carbonate and potassium hydroxide methods. J. W. M.

Group Separation of the Rare Earths by means of Sulphamic Acid. J. Kleinberg, W. A. Taebel and L. F. Audrieth. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 368–369.)—The grouping of the rare earths by means of sodium sulphate into lanthana and yttria earths may be efficiently accomplished by conversion of the earths into sulphamates, and gradual treatment of the ice-cold solution with solid sodium nitrite until the neodymium absorption line 637$m\mu$ disappears.

W. R. S.

Simultaneous Determination of Zirconium and Hafnium by means of Selenious Acid. A. Claassen. (*Z. anal. Chem.*, 1939, **117**, 252–261.)—The author has investigated the precipitation of zirconium as basic selenite (Simpson and Schumb, ANALYST, 1931, **56**, 337), and succeeded in converting it into the normal selenite $Zr(SeO_3)_2$, which is crystalline and of stoichiometrically definite composition. This was determined gravimetrically by ignition (1000° C.) of the precipitate previously dried at 120° to 200° C., and volumetrically by iodimetric determination of the selenious acid after solution of the precipitate in sulphuric acid and sodium fluoride. Hafnium behaves like zirconium, yielding a basic selenite convertible into the normal compound. The gravimetric determination of hafnium in the selenite gives a mean positive error of 1 per cent., the volumetric determination an error of 1·4 per cent. The indirect simultaneous determination of the two elements in the mixed selenite precipitate is carried out as follows:—

The slightly acid solution (maximum, 0·6 *N* sulphuric or hydrochloric acid, but 0·3 *N* for small quantities of zirconium; maximum for nitric acid 0·38 *N*; volume, 400 ml. for 0·1 g. of zirconium) is precipitated in the cold with 2 g. of selenious acid in 10 per cent. solution, heated to boiling, and set aside for 5 to 20 hours on a steam-bath or hot plate until the flocculent precipitate has become dense and crystalline. It is collected in a Jena filtration crucible (G4) for the gravimetric determination or on a paper filter for the volumetric determination, washed eight times by decantation with hot water (hot dilute hydrochloric acid may be used if other elements are present), then with cold water until the washings give no selenium

reaction with starch, potassium iodide and dilute sulphuric acid. For the gravimetric determination, the crucible and its contents are dried at 120° to 200° C. and ignited to constant weight; 0·1000 g. of ZrO_2 yields 0·2801 g. of $Zr(SeO_3)_2$; 0·1000 g. of HfO_2 yields 0·2054 g. of $Hf(SeO_3)_2$.

The volumetric determination is preferable on account of the greater difference between the two conversion factors: 0·1000 g. of ZrO_2 as selenite consumes 64·92 ml. of 0·1 *N* thiosulphate solution; 0·1000 g. of HfO_2 consumes 37·99 ml. The mixed selenite precipitate is rinsed off the filter with a little water and dissolved by gentle heating with 6 ml. of sulphuric acid (1:1) and 10 ml. of 3 per cent. sodium fluoride solution, the warm solution is filtered through the same paper into a 750-ml. conical flask, and the paper is washed with a little dilute acid containing fluoride. The cold solution is diluted (200 to 300 ml.), treated with 10 to 15 ml. of 2 per cent. starch solution, a little sodium bicarbonate and a solution of 4 g. of potassium iodide free from iodate, and titrated after 2 minutes with 0·1 *N* thiosulphate solution. The excess of starch is added for the purpose of keeping the selenium in colloidal solution, thus preventing it from adsorbing iodine. As the titration proceeds, the dark blue solution becomes lighter, then dirty brown; the end-point, a sudden change to pale red, is accurate to one drop, especially if the flask rests on an illuminated pane of opal glass. The volumetric determination gives results reproducible within 0·3 per cent.; the hafnium content in zirconium can be determined within 1 per cent., if an empirical hafnium factor (*i.e.* the theoretical factor multiplied by 1·01) for the thiosulphate solution is used. W. R. S.

Colorimetric Determination of Fluorine with Ferron. J. J. Fahey. (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 362–363.)—The reagent is made up from two solutions: (i) a 0·1 *N* solution of ferric chloride in 0·2 *N* hydrochloric acid, and (ii) a saturated aqueous solution of ferron (7-iodo-8-hydroxyquinoline-5-sulphonic acid). Ten ml. of (i) are mixed with 90 ml. of (ii), and 100 ml. of water. The reagent is quite stable. For the determination of fluorine in rocks, 0·5 g. is fused with 5 g. of sodium carbonate in a platinum crucible until the mass is fluid. The melt is leached overnight with 300 ml. of water in a platinum dish, the extract is heated just to boiling, the residue is washed once with water, returned and boiled for a minute with 100 ml. of water, the liquid is again filtered, and the residue is washed with hot water. The filtrate is treated in a platinum dish with a solution of 1 g. of zinc oxide in 30 ml. of hydrochloric acid (1:3), and boiled, and the precipitate is allowed to settle, collected, and washed in the same way as the preceding precipitate. The filtrate is accurately divided into two parts. One of these is neutralised to methyl orange with hydrochloric acid (1:19); the other is treated with exactly the same amount of acid without the indicator, a solution of 0·5 g. of zinc oxide and 1 g. of ammonium carbonate in 2 ml. of strong ammonia and 10 ml. of water, and gently boiled until no odour of ammonia can be detected, the volume being reduced to about 75 ml. The solution is diluted with 50 ml. of water, stirred and filtered, and the precipitate is washed as described above. The filtrate is made up to 250 ml., a concentration of 0·1 to 1·5 mg. of fluorine in 25 ml. being aimed at; if the rock contains less than 0·2 per cent. of fluorine, 1 g. should be taken, and the final filtrate concentrated to 50 ml.

A 25-ml. portion contained in a 50-ml. beaker, and a standard of the same *p*H and sodium chloride concentration, are treated with 2·00 ml. of reagent and placed in a colorimeter, and the standard is treated with a 0·02 *N* solution of sodium fluoride until its relatively green tint matches the yellow green of the unknown solution, the latter being suitably diluted so that equal volumes are maintained in the two vessels. A difference in tints is apparent with as little as 0·05 mg. of fluorine. With natural waters containing less than 1000 parts of total solids per million, the sensitiveness is twice as great, allowing 0·025 mg. to be determined in a 25-ml. portion. The method may be used with minerals containing up to 10 per cent. of fluorine; beyond this percentage, the error incurred in the colorimetric determination is too great for accurate work. W. R. S.

Microchemical

Examination of Pigments in Painting. E. Bontinck. (*Mikrochem.*, 1939, **26**, 182–188.)—Various tests are examined for the detection of sulphur in lapis lazuli, ultramarine and other mineral pigments which contain sulphur. Feigl's iodine-azide test may give erroneous positive results owing to the presence of sulphur in the oil medium. It is recommended to treat the pigment with 6 *N*-acetic acid on a small silver plate. The resultant black spot of silver sulphide is clearly visible even with a particle 0·005 mm. in diameter. A reaction to distinguish between lapis lazuli and ultramarine is unnecessary, as they are quite distinctive under the microscope. Contrary to what has previously been stated, lapis lazuli is decolorised by dilute acetic acid (by 0·02 *N* acetic acid after 24 hours, but not by 0·01 *N* acetic acid). J. W. M.

Colorimetric Micro-determination of some Phenols. A. I. Matiu, C. Popesco and A. Popesco. (*J. Pharm. Chim.*, 1939, **30**, 49–58.)—The basis of the method, as applied to the determination of phenols, is the formation of a blue colour with a phosphotungstic reagent, followed by the discharge of the colour by titration with potassium ferricyanide solution. The method can be used for the determination of pyrocatechol, hydroquinone, pyrogallol, gallic acid and tannins, but is not applicable to those phenols the reducing power of which is too low for the blue colour to be formed with the phosphotungstic reagent.

Reagents.—(1) *Phosphotungstic reagent*: Ten g. of sodium tungstate, 8 ml. of phosphoric acid (sp.gr. 1·71) and 90 ml. of water are boiled together for 1½ hours beneath a reflux condenser. After cooling, the volume is made up to 100 ml. (2) *Solution of sodium carbonate* (*crystalline*): A 20 per cent. solution. (3) *N*/10 *Ferricyanide solution*: Potassium ferricyanide (1·65 g.) and potassium hydroxide (1·65 g.) are dissolved in 100 ml. of water, and the solution is standardised by Mohr's method (Barral, *Précis d'Analyse Chimique Quantitative*, Paris, 1927, p. 490). (4) *Phenol solution*: About 1 g. in 1000 ml.

Procedure.—A measured volume of the phenol solution is treated with the phosphotungstic reagent and the mixture is made alkaline with the sodium carbonate solution, when there develops a blue colour the depth of which is proportional to the quantity of phenol present. The ferricyanide solution is added

from a micro-burette until the colour is discharged. The following table shows the volumes of phenol solution, phosphotungstic reagent and sodium carbonate solution used, the colour of the liquid at the end-point, and the weight of phenol (in g.) equivalent to 1 ml. of $N/10$ potassium ferricyanide solution.

	Phenol solution ml.	Phospho-tungstic reagent ml.	Sodium carbonate solution ml.	Colour of final liquid	1 ml. of ferri-cyanide solution equivalent to phenol g.
Pyrocatechol					
	0·5	2	30	Pink	0·001376
	1·0	4	30		
	1·5	6	30		
	2·0	8	30		
Hydroquinone					
	0·5	2	30	Pale yellow	0·002752
	1·0	4	30		
	1·5	6	30		
	2·0	8	30		
Pyrogallol					
	0·5	4	20	Yellow	0·001051
	1·0	4	20		
	1·5	4	20		
Gallic acid					
	0·5	4	20		0·001567
	1·0	4	20		
	1·5	4	20		
Tannin					
	0·5	2	20		0·001923
	1·0	2	20		
	1·5	2	20		
	2·0	2	20		
Tannigene					
	0·5	2	20		0·002525
	1·0	2	20		
	1·5	2	20		
	2·0	2	20		
Tannoforme					
	0·5	2	20		0·002058
	1·0	2	20		
	1·5	2	20		
	2·0	2	20		
Quinine tannate					
	0·5	2	20		0·003125
	1·0	2	20		
	1·5	2	20		
	2·0	2	20		

In the analysis of tannin-containing medicinal products such as Tannigene, Tannoforme, and quinine tannate, the product is dissolved, and the tannin is liberated by treatment with sodium hydroxide for the first two and hydrochloric acid for the quinine tannate. E. M. P.

Colorimetric Micro-method for the Estimation of Nitrates. Pesez. (*J. Pharm. Chim.*, 1939, **30**, 112–117.)—In presence of sulphuric acid, nitrates convert nitrobenzene into dinitrobenzene, and the latter condenses with acetone in alkaline solution to give a violet-red colour, the intensity of which is proportional to the amount of nitrate originally taken. Quite small amounts of nitrate can be estimated in this way, the procedure being as follows:—One to 10 ml. of the solution to be tested, depending on the amount of nitrate present, is measured into a porcelain dish and evaporated to dryness after being neutralised by the addition of two drops of ammonia. A drop of nitrobenzene is added to the residue, and then 15 drops of conc. sulphuric acid, care being taken that these fall on to the nitrobenzene and not on to the dry residue of nitrate. The liquid is stirred with a small glass rod for 2 or 3 minutes and is then treated with 5 ml. of acetone; the mixture, after further stirring, is transferred to a stoppered tube, with the aid of a further 5 ml. of acetone. Five ml. of 15 per cent. sodium hydroxide solution are added, and the tube is tightly stoppered, shaken, and allowed to stand for 10 minutes, after which the colour of the solution is compared in a colorimeter with that of a solution prepared in the same way from a known amount of nitrate.

The reaction is sufficiently sensitive to be used for the estimation of nitrate in water, but chlorides must first be removed. Nitrites, however, do not interfere. To 20 ml. of the suspected water are added 2 drops of 20 per cent. sulphuric acid and then a 0·05 *N* solution of silver sulphate, drop by drop, until a drop of the liquid just gives a brown colour with potassium chromate paper. The liquid is then filtered, and exactly half the filtrate, equivalent to 10 ml. of the water, is evaporated to dryness after being neutralised with 2 drops of ammonia. The remainder of the estimation is carried out as described above. Quantities of potassium nitrate ranging from 25 to 50 mg. per litre were estimated with an error of about 10 per cent., even in presence of 200 mg. of sodium chloride per litre.

F. A. R.

Determination of Potassium with Magnesium Dipicrylamine. R. Dworzak and H. Ballezo. (*Mikrochem.*, 1939, **26**, 322–342.)—The method has been adapted to the determination of potassium in mineral waters. It gives satisfactory results in presence of up to 100 times the amount of sodium when excess of wash-liquid, saturated with the potassium salt, is used. The reagent solution (which is also used for washing purposes) is prepared from 19·6 ml. of an approximately 0·25 *N* solution of pure magnesium dipicrylamine, to which is added 2 ml. of a potassium chloride solution containing 1 mg. per ml.; the mixture is left for 4 hours and diluted with 50 ml. of water, and may be used the following day. The reagent is filtered immediately before use. A porcelain crucible is used for the precipitation: a porcelain filter-stick for the filtration. It is advisable to use a 50 per cent. excess of reagent. The precipitate should be cooled for 7 hours and then left for 3 days before filtering. It is then washed with the reagent solution and finally with ether and dried at 85° to 95° C.

J. W. M.

Microchemical Reactions for Scandium. G. Beck. (*Mikrochim. Acta*, 1937, **2**, 9–12). The following reagents are particularly suitable for tests for scandium in minerals:—morine, which gives a green fluorescence extinguished by alkali fluorides; alizarine sodium sulphonate in slightly acid solutions, which gives a precipitate; aurine tricarboxylic acid, which gives a red precipitate soluble in ammonia to form a yellow-brown solution (the precipitate formed by aluminium is not soluble in ammonia). Luteo cobalt nitrate gives a yellow-brown crystalline precipitate of $[Co_2(NH_3)_6][ScF_6]$ with complex solutions of scandium fluoride. This reagent also reacts with aluminium, beryllium and zirconium in acid solution to form amorphous precipitates; in ammonium carbonate solution, beryllium does not react, and zirconium gives an amorphous precipitate. The crystals of the aluminium and scandium compounds are readily distinguished. Magnesium in ammoniacal solution forms an easily recognisable crystalline product with the cobalt reagent. J. W. M.

Reviews

THE PHASE RULE AND ITS APPLICATIONS. By ALEXANDER FINDLAY, M.A., D.Sc., F.I.C., revised with the assistance of A. N. CAMPBELL, D.Sc., F.I.C. Eighth Edition. Pp. xv + 327, with 163 figures. London: Longmans, Green & Co. Ltd. 1938. Price 12s. 6d. net.

As a guide and means of classification in the study of chemical equilibria in systems other than those which are wholly gaseous, the Phase Rule is still of particular value. Professor Findlay's exposition, first published in 1904 and long regarded as the standard English text-book on the Phase Rule, has been brought up to date again (editions were reviewed in THE ANALYST, 1923, 575; 1928, 244), and work published as late as 1938 is included. References to applications of X-ray analysis in Phase Rule problems are welcome additions, but it is to be hoped that in the next edition a more even balance will be struck between the applications to "non-metallic" systems and "metallic" systems, as the latter seem somewhat neglected in view of the present importance of alloys.

There are a few slips, such as a reference (p. 34) to the Appendix dealing with the experimental determination of the transition point, which has been omitted from the present edition, and it is a little confusing to speak of heated mercury *subliming* through a layer of liquid bromonaphthalene (p. 92), in view of the implied definition of sublimation (p. 21). However, the analyst will find underlying principles to guide him in some of his problems, as in converting insoluble systems into soluble systems by fusion (p. 287), and a word of warning that different substances with identical melting-points do not necessarily depress each others' melting-points on admixture (p. 124).

Notwithstanding such minor criticisms, this edition is a worthy successor to its predecessors. J. G. A. GRIFFITHS

MAY'S CHEMISTRY OF SYNTHETIC DRUGS. By PERCY MAY, D.Sc. (Lond.), F.I.C., and G. MALCOLM DYSON, Ph.D., F.I.C., A.M.I.Chem.E. 4th Edition. Pp. xii + 370. London: Longmans, Green & Co. Ltd. Price 21s.

Of the nature of drug action very little is known with certainty, but theories have been advanced from time to time, such as those of Ehrlich, who makes an analogy with dye action, and of Loew, who correlates physiological activity with the chemical affinity of a drug for aldehyde and amino groups, and the more modern theory of biochemical interference, which postulates modification of enzyme activity as the controlling factor. On the other hand, the manner in which a drug reaches the seat of its action is better understood, being in a measure dependent on physical properties, particularly solubility. Overton and Meyer, for example, long ago showed that a close relationship exists between the effectiveness of narcotics and their distribution coefficients between lipoid substances and water. It is with such ideas that the authors of this book are concerned in the three introductory chapters, which summarise the principles by which the chemist is guided when synthesising a new drug.

Chapter II is devoted to the physiological effects which are frequently associated with different atoms and groups, as for example, the action, on the central nervous system, of ethyl groups when introduced into a suitable molecule. A list of generalisations, known as Schmiedeberg's Rules, is followed by a discussion of the more important atoms and groups from this point of view, including the effect of unsaturation and stereoisomerism.

The subject of the next section—the chemical changes which drugs undergo in the organism—is of considerable importance, since a study of the elimination products of a drug may give a clue to its mode of action and even indicate the manner in which its structure can be modified in order to decrease its toxicity. As is mentioned later in the book, the discovery that aniline and its simple derivatives are eliminated from the body as a compound of *p*-aminophenol and glycuronic acid led eventually to the synthesis of phenacetin.

Following this general treatment is the main subject matter of the book which, owing to its diversity, offers some difficulty of presentation. The authors have not attempted a hard and fast systematic treatment throughout, but have chosen for their chapter headings the strongest common relationships between the substances described therein. Thus sometimes similar physiological effect is the keynote, as, for example, "Narcotics and General Anaesthetics," and at other times common chemical origin ("Adrenaline and other Derivatives of Ethylamine"). In fairness it must be said that this method produces a good sequence within the chapters, and possibly a more rigid classification would have produced a less readable book.

Since several of the natural alkaloids and many "artificial" ones have now been synthesised, this branch of the subject receives a considerable share of treatment. After an introductory chapter dealing with active groupings in alkaloidal structure, there follows an account of quinine and its derivatives, the alkyl hydro cupreines, and various quinine compounds of therapeutic value. Substitutes for quinine, such as Plasmoquin, are also described. Next we have

the properties and syntheses of atropine and the tropeines, followed by cocaine and its substitutes, the eucaines, stovaine, novocaine and other local anaesthetics. Although morphine itself has never been synthesised, many attempts have been made to prepare derivatives of it and to produce compounds containing similar groupings. In view of this, a résumé is given of the chemistry of morphine and its related alkaloids including members of the apomorphine group. Narcotine, papaverine, hydrastine and others of the isoquinoline group receive similar treatment and, wherever possible, full syntheses are indicated with references to the original work.

Because of the powerful physiological effect of many derivatives of ethylamine, these compounds have been grouped together under one heading and include adrenaline, ephedrine, benzedrine, histamine and similar bodies.

The most notable expansion of this edition is due to the addition of a chapter on Hormones and Vitamins. To condense such a subject into twenty pages was a bold undertaking, but the authors have at least succeeded in producing a useful summary of some of the results achieved. Syntheses of vitamins A, B_1, B_2 and C are given, and mention is made of the recent success in producing α-tocopherol (vitamin E). The hormones are represented by thyroxin and the sex hormones. It is obviously impossible to give more than a brief outline of the latter in such limited space, and the treatment has been confined to their origin, mode of action and relationships one to another. A useful diagram showing the mechanism of the action of the female sex hormones is given, and mention is made of the recently discovered synthetic derivatives of stilbene, whose activity actually exceeds that of oestrone. A list of references would have been a useful addition here for the reader who may require further information.

Organic antiseptics include the therapeutically active dyes (triphenylmethane series, trypan blue, etc.), the complex ureas (Bayer 205, S.U.P.), the sulphonamides and acridine derivatives (acriflavine, atebrin).

Compounds containing metals in combination are treated in two sections—the first dealing with those of mercury, silver and gold, and the second with those of arsenic, antimony and bismuth. These include most of the well-known general antiseptics and anti-syphilitics and need not be further commented upon here.

It is impossible in a review of this length to touch upon everything in the book; let it suffice to say that the authors have omitted very little of their legitimate subject matter. A justified criticism would appear to be that they have at times gone outside the scope of the title.

The book will be of considerable use to the organic chemist interested in the synthesis of drugs, and a source of stimulating ideas to all chemists, on account of the many ingenious synthetic methods abstracted from the freely-quoted patent literature. It will also be of considerable use as a reference book in view of the comprehensive index that it possesses. Finally, the account of many beautiful syntheses, invariably represented by graphic formulae, will be a useful aid to the student and save him much weary searching of the textbooks.

G. E. H. SKRIMSHIRE

CASEIN AND ITS INDUSTRIAL APPLICATIONS. By EDWIN SUTERMEISTER, S.B., and FREDERICK L. BROWNE, Ph.D. Second Edition. Pp. 433, with 35 Tables and 50 Figures. New York: The Rheinhold Publishing Corporation; London: Chapman & Hall, Ltd. 1939. Price 32s. 6d. net.

A new edition of Sutermeister is something of a major event in the casein world. The first edition appeared in 1927, when the industry was, relatively speaking, in its infancy, and at that time the book was more than a mere review of current practice and literature. It carried out invaluable pioneer work in pointing out the possibilities of the industry and emphasising the need for scientific control. In 1927, as now, the book impressed by virtue of its reasoned judgment. It has helped the development of casein by countering the somewhat extravagant claims made from time to time.

Even if in some degree the casein industry has not fulfilled the promise of its youth, it has developed to an extent which has made sections of the early Sutermeister begin to date. Eight of the original eleven contributors have collaborated in the new edition and parts of the book have been completely re-written. Parts are new not only in matter but also in emphasis. For example, in the United States the whole attitude towards casein manufacture has changed. When the first edition of the book appeared, casein was largely a by-product of the creameries, made in the simplest and cheapest plant available, with little control or scientific method. It is not surprising that the variable nature of casein made under such conditions led to a prejudice in favour of competitive materials and placed the industry under a handicap still felt to-day. Now casein of uniformly high quality is so widely available that material made by the old "hit or miss" methods is difficult to sell. Sutermeister can claim much of the credit for this improvement by the emphasis laid on scientific control in 1927.

Naturally the book has a strong American colouring, and statistics are mostly confined to the States. This colouring may be misleading, for some of the statements are not applicable to the British Empire. At any rate in the States, the vat method of self-souring would appear to have receded in importance in favour of "continuous" processes, and the latter, mentioned more or less in passing in the earlier edition, now receive detailed description. One "continuous" process, the Sheffield method of hydrochloric acid precipitation, is described at considerable length and would appear to be perhaps the chief development in manufacturing technique since 1927.

Although the book has been considerably enlarged, its fundamental honesty becomes apparent as much by its omissions as its additions. On carefully comparing sections, the disappearance of many minor applications of casein, which were pious hopes in 1927, but failed to become established on any appreciable scale, is noteworthy.

According to statistics quoted, the manufacture of casein in the States in 1937 was about five to eight times what it was in the immediate post-War years, and the consumption about three times. By far the greater part of this, possibly over 70 per cent., was used in paper coating. Plastics claim over 10 per cent. as second on the list, and the major usage in this field is in the manufacture of buttons. The chapter on paper-making contains little of novelty, and here the improvement

in the quality and reliability of casein has been the largest factor in its extended use. The chapter on plastics admirably reflects the changes of the last ten years, and the increase of the bibliography from 66 references in 1927 to over 400 in the new edition tells its own story. Even if the employment of casein in the manufacture of buttons stands out most prominently, other applications are still more than mere optimism, and the battle with phenol resins has not gone entirely one way.

The fascinating new development of "Lanital," synthetic textile fibres from casein, is fully described and, although the future of this product cannot yet be predicted, it would appear to have wide possibilities and is already being made on a fairly large scale in Italy.

The section on glues has been carefully revised and some valuable observations on "working life" added. Casein paints have developed markedly since the earlier edition of the book, and paste paints are virtually an innovation which has become firmly established since 1927. The chapter on paints has also been enlarged, and the bibliography both on glues and on paints considerably extended.

The chapter on the testing and analysis of casein has been brought up to date, and has been placed in a more prominent position in the book instead of being relegated to the end. The notes on ash determination are of special interest, even if the relationship between proximate ash-content and viscosity may be open to doubt.

Lastly, it remains to congratulate the authors and the publishers on the improved appearance of the book, the excellent quality of the illustrations and the increased clarity of the diagrams and tables. It is not unreasonable to assume that improvements in the quality of casein have played a part in this!

E. W. PATES

ORGANIC CHEMISTRY. Professor PAUL KARRER. Translated from the latest German edition by A. J. MEE. Pp. xx + 902. Elsevier Publishing Co., Ltd., Amsterdam and London. 1938. Price 45s.

In the preface the author states that his aim was to provide students with a textbook of organic chemistry of medium size which would give them a survey of the ever-increasing body of facts, and it may be said at once that he has succeeded in an admirable and praiseworthy manner.

In dealing with the main body of the subject, the historical and usual division into aliphatic, carbocyclic and heterocyclic compounds has been retained, although not slavishly followed. In each section the compounds are regarded as derivatives of the hydrocarbons and have been arranged, as far as possible, according to their functional groups.

As might be anticipated from a survey of the investigations in which Professor Karrer has played so brilliant a part, considerable prominence is given to the chemistry of naturally occurring substances, and various biochemical topics are dealt with in some detail. As some of the most striking and fruitful developments in the whole of organic chemistry in recent years have lain in the borderland of chemistry and biology, this emphasis on the biological aspect enhances in a very real way the value and utility of this book to the present-day student.

Although the number and variety of compounds dealt with are both large and

extensive, the book is eminently readable; it is far from being of the dictionary type and deals with synthetical methods in considerable detail.

By way of criticism it may be pointed out that the application of the principles of the electronic theory of valency receives scant and cursory treatment and is not even mentioned in the detailed index; it is surprising also to find numerous structural formulae in which nitrogen is represented as a penta-covalent element and many in which sulphur functions as a hexa-covalent element. The physico-chemical side of the subject is referred to here and there in an incidental and almost casual manner.

Whilst these omissions, from a textbook intended for the general student, of some of the more important developments on the theoretical side result in a certain loss of balance in the presentation of the subject, they do not seriously impair the general excellence of the work.

English students suffer from no lack of valuable monographs dealing with the theoretical and physico-chemical aspects of organic reactions, and they should be grateful that Professor Karrer has emphasised those sections of chemistry to which the term organic was originally applied.

The volume concludes with numerous tables of data which are both useful and interesting.

The translation has been well done and the English version reads smoothly and easily. The publishers have done their part well in the general make-up of the book; the paper is opaque, the type clear and legible and the binding strong and substantial.

It is to be regretted that the high cost may hinder the wide circulation that the book deserves and ought to have. J. KENYON

ANLEITUNG ZUR ORGANISCHEN QUALITATIVEN ANALYSE. By H. STAUDINGER and W. KERN. 3rd Edition. Pp. xvi + 157. Berlin: Julius Springer. 1939. Price RM.6.90.

This well-known textbook has undergone little essential change since the previous edition of 1929. It has, however, been revised and brought up to date by the inclusion of much new material. Thus one finds descriptions of the use of Girard's reagent for aldehydes and ketones, dinitrochlorobenzene for phenols, anthraquinone-β-carboxylic acid for alcohols, di-*p*-dimethylaminophenyl-carbodi-imide for acids, and other reagents of a similar nature.

This is not a textbook that can be used by itself for the complete identification of individual substances. It is a guide or key (Anleitung) to assist the student in classifying an unknown compound, so that, having put it into the right pigeon-hole, he will be able to identify it more easily. For this final stage, the student is referred to Kempf and Kutter's *Schmelzpunktstabellen zur organischen Molecularanalyse*. Dr. Staudinger's system of classification consists in dividing substances first into two groups, namely, those that boil below 160° C. and those that boil above that temperature, and then each group into five sub-groups according to the behaviour towards water and ether, and finally each sub-group into acids, phenols, bases and neutral substances. Such a scheme has obvious advantages, though it is easy to imagine that a substance might turn up in two of the ultimate divisions, because

its properties happen to fall along the arbitrary boundary-line dividing two of the sub-groups. But doubtless the author has allowed for this possibility.

The book is furnished with a good index of substances, but not with an index of reactions. This is unfortunate, as the preparation of derivatives is a particularly strong feature of the book, and the absence of an index renders reference to these a troublesome matter. F. A. ROBINSON

Publications Received

CRYSTAL CHEMISTRY. By R. C. EVANS. Pp. xi + 388. Cambridge University Press. 1939. Price 18s. net.

ORGANIC SYNTHESES. J. R. JOHNSON, Editor-in-Chief. Vol. XIX. Pp. 105. New York: Wiley & Sons. London: Chapman & Hall, Ltd. 1939. Price 8s. 6d. net.

ESSENTIALS OF PHYSIOLOGICAL CHEMISTRY. By A. K. ANDERSON. Pp. xi + 323. London: Chapman & Hall, Ltd. 1939. Price 13s. 6d. net.

USES AND APPLICATIONS OF CHEMICAL AND RELATED MATERIALS. By T. C. GREGORY .Pp. vi + 665. New York: Rheinhold Publishing Co. London: Chapman & Hall, Ltd. 1939. Price 50s. net.

THORPE'S DICTIONARY OF APPLIED CHEMISTRY. 4th Ed. Vol. III.—Chemical Calculations—Diffusion. Pp. xxiii + 608. London: Longmans, Green & Co. Ltd. 1939. Price 63s. net.

LAVOISIER. By J. A. COCHRANE. Pp. 264. London: Constable & Co., Ltd. Re-issue. Price 3s. 6d. net.

A LABORATORY MANUAL OF QUALITATIVE ANALYSIS. By J. H. YOE. Pp. 219. New York: Wiley & Sons. London: Chapman & Hall, Ltd. Price 12s. 6d. net.

THE WAR GASES: CHEMISTRY AND ANALYSIS. By MARIO SARTORI. Translated from the Second Italian Edition by L. W. MARRISON. Pp. xii + 360. London: J. & A. Churchill, Ltd. 1939. Price 21s.