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### NOTES ON THE MEASUREMENT OF HYDROGEN ION CONCENTRATION.

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(*Read at the Meeting, May* 4, 1921.)

The determination of absolute acidity or hydrogen ion concentration has not yet found its way into many analytical laboratories, mainly on account of the expense of the apparatus which is usually considered necessary. The object of this paper is to indicate how the electrical measurement of acidity can be carried out with comparatively simple and inexpensive apparatus with a degree of accuracy comparable to that attained by titration methods.

Theoretical Basis of the Method.—The elementary theory of the method can be stated quite briefly. If a rod of metal be dipped into water, a minute quantity of the metal goes into solution in the form of metallic ions bearing a positive charge. The metal therefore becomes negatively charged with reference to the water. The magnitude of the potential difference set up between metal and liquid depends upon the solution pressure of the metal in question. The quantity of metal passing into solution is extremely small, since electrostatic attraction is almost immediately set up between the negatively charged metal and the positive ions in solution, and this prevents further solution of the metal. If the solution already contain a salt of the metal, there is a tendency for the positive metallic ions in solution to separate out on the metal, which therefore becomes positively charged with reference to the solution.

The actual difference of potential between metal and liquid is the resultant of these two opposing forces. While the solution pressure is always constant for one and the same metal, the tendency for the reverse operation to occur varies with the number of metallic ions present in solution. Thus the electric potential of a metallic electrode in contact with a solution of one of its salts is a measure of the concentration of metallic ions in the solution.

When hydrogen is absorbed by finely divided platinum, it behaves in many ways as a metal and exerts a definite solution pressure. Platinum itself has a negligible solution pressure, so that an electrode of platinum coated with platinum black and saturated with hydrogen behaves electrically as if it were metallic hydrogen. The difference of potential set up when such an electrode is dipped into an aqueous solution is therefore a measure of the concentration of hydrogen ions in that solution.

MEASUREMENT OF DIFFERENCE OF POTENTIAL.—It is a difficult matter to measure the absolute difference of potential between a solid electrode and a liquid. This difficulty can be overcome by indirect methods. The method usually adopted is to combine the electrode, through the medium of an intervening vessel containing an appropriate liquid, with a standard electrode of known potential, and to measure the electromotive force of the resulting cell. This standard electrode may consist of platinum saturated with hydrogen and in contact with a solution of known hydrogen ion concentration. In the normal hydrogen electrode, to which all measurements are eventually referred, the solution contains 1 grm. of ionised hydrogen per litre. It contains slightly more hydrochloric acid than the ordinary normal HCl solution, owing to the fact that the dissociation of the acid is not quite complete. Several other solutions of known definite hydrogen ion concentration have been used as standards, but it is more convenient to employ a decinormal calomel electrode. In this the electrode consists of mercury and the liquid is a $\frac{N}{10}$ potassium chloride solution saturated with calomel. The difference of potential between the mercury and solution is 0·613 volt, the mercury being positive and the solution negative.

If this electrode be coupled up with a hydrogen electrode, the current tends to flow outside the cell from the mercury to the platinum, and if the hydrogen electrode be a normal one, the difference of potential between the two electrodes is 0·338 volt. With solutions of lower hydrogen ion concentration the potential difference is, of course, greater than this, since more hydrogen tends to pass from the platinum into the solution, and the platinum becomes more negative with reference to the solution. For some purposes it is preferable to use a calomel electrode made up with $\frac{N}{1}$ potassium chloride, or even a saturated potassium chloride solution. With these electrodes the E.M.F. of the cell has a different value.

RELATIONSHIP OF E.M.F. AND HYDROGEN ION CONCENTRATION.—The following table shows the simple linear relationship which exists between the E.M.F. of the cell when using a $\frac{N}{10}$ calomel electrode, and the strength of the solution in respect of hydrogen ions:

| E.M.F. against $\frac{N}{10}$ Calomel Electrode Volts. | Normality of Solution in Respect of Hydrogen Ions. | $P_H^+$ |
|---|---|---|
| 0·338 | $\frac{N}{1}$ | 0 |
| 0·396 | $\frac{N}{10}$ | 1 |
| 0·453 | $\frac{N}{100}$ | 2 |
| 0·511 | $\frac{N}{1,000}$ | 3 |
| 0·569 | $\frac{N}{10,000}$ | 4 |
| 0·626 | $\frac{N}{100,000}$ | 5 |
| 0·684 | $\frac{N}{1,000,000}$ | 6 |
| 0·742 | $\frac{N}{10,000,000}$ | 7 |
| 0·800 | $\frac{N}{100,000,000}$ | 8 |
| 0·857 | $\frac{N}{1,000,000,000}$ | 9 |
| 0·915 | $\frac{N}{10,000,000,000}$ | 10 |
| 0·973 | $\frac{N}{100,000,000,000}$ | 11 |
| 1·030 | $\frac{N}{1,000,000,000,000}$ | 12 |

Instead of expressing the hydrogen ion concentration of a solution as, *e.g.*, $\frac{N}{1,000}$, the logarithm of the denominator, termed $P_H^+$, is generally used. Thus for a solution of $\frac{N}{1,000}$ strength in respect of hydrogen ions, $P_H^+$ would be equal to 3, since 3 is the logarithm of 1,000. At the point of absolute neutrality the concentration of hydrogen ions, due to the dissociation of water into $^+_H$ and $_{OH}^-$ ions, corresponds to $P_H^+ = 7{\cdot}12$ at 18° C., or $\frac{N}{13,160,000}$, and the E.M.F. against the $\frac{N}{10}$ calomel electrode is 0·748 volt. As we get into the region of alkalinity, the hydrogen ion concentration becomes still smaller—*i.e.*, the value of $P_H^+$ greater, since, according to the laws of mass action, the product of the concentration of $^+_H$ and $O_H^-$ ions must be constant. Thus even the most strongly alkaline solutions will show a definite, though extremely minute, concentration of hydrogen ions.

Comparison with Titration Methods.—The values for acidity obtained by this method are not the same as those given by titration, owing to the varying degree of electrolytic dissociation shown by different acids. Thus a $\frac{N}{10}$ solution of acetic acid gives the same result on titration as $\frac{N}{10}$ hydrochloric acid, since each contains a chemical equivalent of the respective acid in 10 litres. The hydrochloric acid, however, is dissociated to the extent of 91 per cent. into hydrogen and chlorine ions, while only 1·3 per cent. of the acetic acid is in the ionic condition. The hydrogen ion concentration of $\frac{N}{10}$ hydrochloric acid is in the neighbourhood of $P_H^+ = 1$, while that of $\frac{N}{10}$ acetic acid is $P_H^+ = 2{\cdot}89$, and for $\frac{N}{10}$ solutions of weaker organic acids the hydrogen ion concentration is still lower. A single determination of this value cannot therefore take the place of a titration unless the degree of dissociation of the acid be known, but there are three directions in which the method may be of value in analytical work.

1. The absolute acidity, quite apart from the titration value, may afford an indication of the extent to which a particular substance is likely to act on the metal or other material of the container. The solvent action of various foods upon tin containers and upon lead-glazed earthenware cooking vessels are cases in point.

2. When combined with a titration, the method may give information as to the nature of the acid in solution—that is to say, whether it is a mineral acid or an organic acid, or a mixture of the two. Vinegar adulterated with sulphuric acid would be a case in point.

3. In the titration of dark-coloured solutions, where ordinary indicators cannot be used, portions may be withdrawn at intervals, and successive determinations of the hydrogen ion concentration made until the value $P_H^+ = 7{\cdot}12$, corresponding to complete neutrality, is reached.

Poggendorf's "Compensation" Method.—The simplest method of measuring the potential difference is the so-called "compensation" method of Poggendorf, shown diagrammatically in Fig. 1. A is an accumulator, W a thin wire 1 m. in length of 10 to 20 ohms resistance, C the cell of which the E.M.F. is to be measured, S a sliding contact, and E an electrometer or galvanometer connected with a key K. Between the two ends of the wire W there is a constant and regular fall of potential. If we assume that between P and $P^1$ there is a difference of potential of 2 volts due

to the accumulator current, then at a point X, three-quarters of the way along the wire from $P^1$, the potential difference between X and $P^1$ is $\frac{3}{4} \times 2$, or 1·5 volts. If the E.M.F. of the cell C be exactly 1·5 volts, and the sliding contact S be placed at this point, the opposing E.M.Fs. will neutralise each other, and no current will flow through the electrometer E when the key is depressed. Whatever the E.M.F. of the cell C, so long as it is less than 2 volts, a point can be found, by moving the sliding contact S along the wire, at which no current will flow through E. Having found this point, we substitute for C a normal cell $C^1$ of known E.M.F., and ascertain again the point at which no current flows. If we call these two points X and $X^1$, then the unknown E.M.F. of the cell is found by simple proportion:

$$C : C^1 = P^1X : P^1X^1.$$

For the most accurate work the resistance wire is replaced by a potentiometer or resistance box, and a delicate galvanometer is used to ascertain the point at which

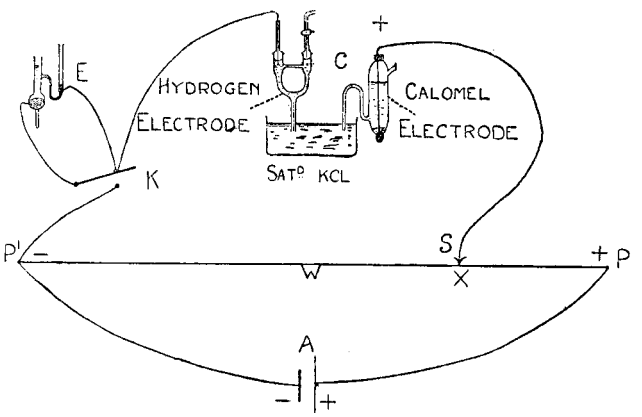


FIG. 1.—DIAGRAM OF POGGENDORF'S COMPENSATION METHOD.

no current flows. The normal cell used for comparison is specially constructed, and is usually calibrated at the National Physical Laboratory. The temperature at which the measurements are made is controlled by immersing the cells in a thermostat.

NORMAL CELL AND ELECTROMETER.—These refinements are not necessary for ordinary work, where an accuracy of 0·002 to 0·003 volt is quite sufficient. A normal cell with poles of cadmium amalgam and mercury showing a constant E.M.F. of 1·0186 to 1·0187 volts at 18° C. is easily made in the laboratory, and will retain its E.M.F. unchanged for many years.

A capillary electrometer, when certain precautions are taken, gives quite satisfactory results, and is easily constructed by any glass-blower. The most important points in preparing this electrometer for use are to get the interior of the capillary perfectly clean by treatment with hot chromic acid, and to use pure mercury and dilute sulphuric acid which has previously been well shaken up with mercury and allowed to stand in contact with the metal for some time. The electrometer is connected with a key (K in Fig. 1) so arranged that its two poles are

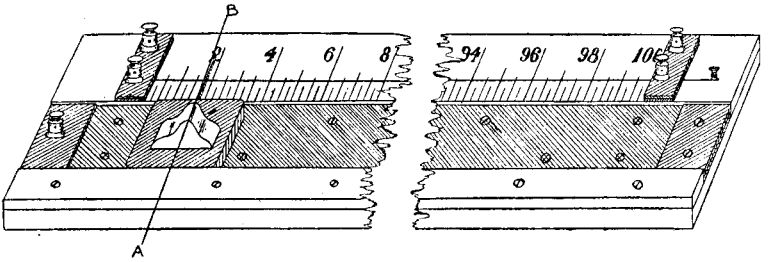


FIG. 2*a*.—MEASURING BRIDGE.

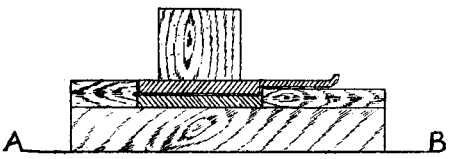


FIG. 2*b*.—BRIDGE CONSTRUCTION.

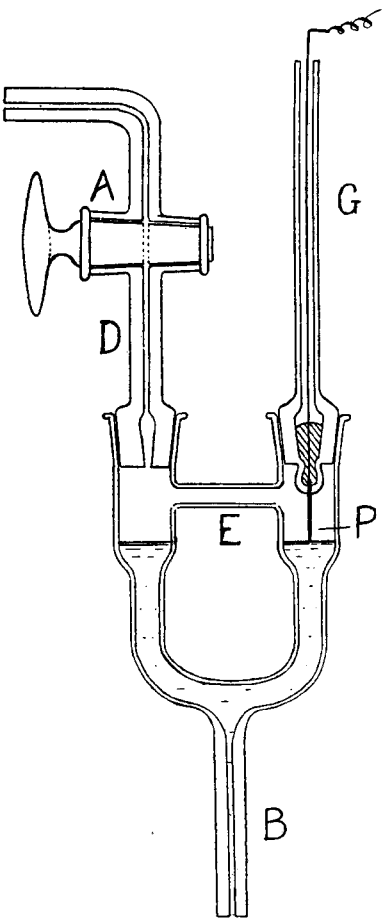


FIG. 3.—HYDROGEN ELECTRODE.

always short-circuited through the key except at the moment when the key is depressed during the taking of a reading.

The $\frac{N}{10}$ calomel electrode is also readily made in the laboratory. It is not possible in a paper of this character to describe the construction of these pieces of apparatus with the necessary completeness of detail. They are fully described and figured in Ostwald's "Physiko-Chem. Messungen," 1902, pp. 333-342, 361-364, 381-383, and later editions. It should be noted that it is electromotive force, and not current, which is measured by this method. While current flows continuously through the accumulator circuit, the electrometer circuit is kept open except during the fraction of a second required for an observation. If this circuit be allowed to remain closed for any length of time, there will be danger of polarisation occurring in the cells and electrometer, leading to irregular results.

Resistance Wire.—As regards the resistance wire and the hydrogen electrode, I have found the special forms shown in Figs. 2*a*, 2*b*, and 3 the most satisfactory.

The former, which was made by Mr. W. A. Godby in my laboratory, consists of a thirty-four gauge "Eureka" wire of approximate resistance 10 ohms per yard, and exactly 1 m. in length, stretched on a board above a metre scale. The two ends of the wire are in contact with brass terminals. The sliding contact is a copper needle passing under the resistance wire and fixed to a metal plate which slides along a brass strip laid the length of the board. Connection between the sliding contact and the electrometer circuit is made by a terminal at one end of the brass strip. The resistance of the brass strip being "nil," this arrangement is equivalent to attaching the wire of the electrometer circuit direct to the sliding contact, and has the advantage that the wire of the circuit does not get into the way when the slide is moved. If desired, the resistance wire can be calibrated by comparison with standard resistances or by Strouhal and Barus' method (Ostwald's "Physiko-Chem. Messungen," 1902, p. 350), but I have not found this necessary, except for very accurate work.

Hydrogen Electrode.—The construction of the hydrogen electrode is shown in Fig. 3 reduced to approximately three-fifths diameter. The U-tube is closed by two ground-in stoppers, one of which carries a capillary tube D, furnished with a cock A, while through the other passes a wider tube G, with a short piece of stout platinum wire P fused into its lower end. Before use, this wire is coated with platinum black. This is done by immersing the clean wire in 2 to 3 c.c. of a 3 per cent. platinum chloride solution containing a minute trace of lead acetate, and passing the current from an accumulator through the liquid. The wire which is to be coated is made the cathode and another piece of platinum wire the anode. Electrical contact with the fused-in wire is secured by an amalgamated copper rod dipping into a drop of mercury in the bottom of the tube G. After the current has passed for two or three minutes the wire has become sufficiently coated with platinum black. It is then removed from the solution and washed with distilled water. In order to remove the last traces of platinum chloride the electrolysis is repeated for a few minutes, dilute sulphuric acid being used instead of platinum chloride. This has the effect of reducing any residual platinum chloride to platinum. The electrode is then again washed with distilled water and replaced in the U-tube.

To carry out a measurement with this electrode, the U-tube is filled with the liquid to be examined by opening the cock A and drawing the liquid up through the capillary B until both sides of the U-tube are completely filled. Electrolytic hydrogen, of which only a few cubic centimetres are required for each determination, is then passed in through the capillary D, care being taken that no air gets in as well. The hydrogen is allowed to displace the liquid just so far that the tip of the platinum wire P touches the surface of the liquid. This is an important point, as it is found that if the platinum be more fully immersed it is difficult to get constant readings in a short time. The form of the U-tube, with its cross connection E, allows of its being tilted to the required angle for contact to be established without having to adjust the volume of the hydrogen.

When the electrode has been filled it is placed in a holder, and the end of the capillary tube B dipped into a vessel containing saturated potassium chloride. The siphon tube of the calomel electrode is also dipped into the same solution, and the two electrodes connected up as shown in Fig. 1. Care must be taken that the positive and negative poles correspond to those of the accumulator, so that the two currents are opposed in direction.

Potassium Chloride Solution as Connecting Liquid.—The object of using a saturated solution of potassium chloride as connecting liquid is to avoid errors due to diffusion potential. If two solutions be brought into contact with each other, there is a tendency for ions to migrate or diffuse from one solution to the other across the boundary line. Thus, if a hydrogen chloride solution be brought into contact with a potassium chloride solution, diffusion of hydrogen, chlorine, and potassium ions will occur in both directions in amount proportional to their relative concentration in the two liquids. The migration velocities of the different ions vary considerably, that of hydrogen being much higher than any of the others. Hydrogen ions will therefore diffuse into the salt solution at a greater rate than potassium ions can move in the reverse direction, and the salt solution will become positively charged with reference to the HCl. The potential difference thus set up will, unless allowed for, cause an error in the reading when the circuit is closed. If the two solutions be separated by a highly concentrated solution of potassium chloride in which the migration velocities of anion and kation are approximately the same, the diffusion of hydrogen, relatively to that of the other ions present, is reduced to a negligible amount, and the error from this source is avoided.

The cell of which the E.M.F. is to be measured is therefore the following: ($Pt.H_2$ : solution : saturated KCl : ($\frac{N}{10}$ KCl : $Hg_2Cl_2$ : Hg).

When the point on the resistance wire has been found at which no current passes on depressing the key of the electrometer, the connections are changed over to the standard cell and another reading taken. The E.M.F. of the first cell is found by simple proportion, and the hydrogen ion concentration of the solution can be ascertained by interpolation from the table given above.

Accuracy of the Method.—In comparing the accuracy of the method with ordinary titration we may take the case of $\frac{N}{10}$ hydrochloric acid. In a titration one will take, say, 25 c.c. of the liquid, and titrate with $\frac{N}{10}$ sodium hydroxide solution, with an accuracy of 0·1 c.c., or 1 in 250. In the electrical method a $\frac{N}{10}$ hydrochloric

acid solution, of which only 5 to 10 c.c. are required, gives an E.M.F. of 0·398 volt when coupled up with a $\frac{N}{10}$ calomel electrode. The E.M.F. at absolute neutrality is 0·748 volt, the difference between the two being thus 0·350 volt. If the potential difference between the two ends of the resistance wire be reduced to, say, 1·5 volts by the insertion of a small coil of thin wire in the accumulator circuit, 0·350 volt will correspond to a length of $\frac{0{\cdot}3}{1{\cdot}5}\frac{5}{0}$ m. on the wire, or 233 mm. With the apparatus described it is possible to read to 0·5 mm., but in ordinary work the error, unless the wire is calibrated and the temperature of the electrodes carefully regulated, will usually amount to 0·002 to 0·004 volt, corresponding to 1·5 to 3 mm. on the wire. This represents a degree of accuracy of 1 in 100 to 200, as compared with 1 in 250 by titration.

It is more particularly with weak organic acids that the method is of the greatest value. Such solutions can often not be titrated satisfactorily. The colour change of the indicator is too gradual, and the type of indicator employed has a great influence on the result. The electrometric method gives us exact values for acidity or alkalinity comparable with each other, whatever the nature of the solutions examined.

Control Test.—The accuracy of the measurements can be controlled by a test carried out on a solution of known hydrogen ion concentration. A convenient solution for this purpose is: 10 c.c. *N* sodium hydroxide solution; 20 c.c. *N* acetic acid; and 70 c.c. distilled water.

If this solution be introduced into the hydrogen electrode vessel and coupled with a $\frac{N}{10}$ calomel electrode, the E.M.F. of the cell should be 0·6045 volt at 18° C. Several other such solutions are given by G. S. Walpole (*Biochem. J.*, 1914, **8**, 628-640). Walpole has also described a simple arrangement for introducing hydrogen into the electrode which is particularly convenient for electrometric titration, and has prepared a useful chart giving the more important data for different standard solutions and indicators (*Biochem. J.*, 1913, **7**, 410; 1914, **8**, 131).

Liquids containing Dissolved Gases.—Liquids containing gases in solution require special consideration, according as the gas is active in an electromotive sense or not. To the former class belong free chlorine and free ammonia. If these be present in the liquid and liable to be given off into the hydrogen atmosphere, the method cannot be used. The platinum will behave partly as a hydrogen electrode and partly as a Cl or $NH_4$ electrode, and the potential difference will be dependent not only upon the concentration of H-ions, but also upon that of Cl or $NH_4$ ions in the liquid. Carbonic acid gas is not active in the same way, but errors may be produced by the escape of carbon dioxide from the liquid into the hydrogen atmosphere. The surface layers of the liquid thus become gradually more alkaline, owing to escape of carbon dioxide, and the reading will not become constant until equilibrium is established. This question is fully discussed by Walpole (*Biochem. J.*, 1913, **7**, 424-426). With the U-shaped electrode the manipulations necessary to obtain gaseous equilibrium between the solution and the hydrogen are easily carried out. The error due to the reduction in the partial pressure of the hydrogen by the presence of carbon dioxide is small, and may be neglected.

Details and Precautions.—A few practical points about the apparatus may be mentioned. All connecting wires should be well insulated, and constructed of stout

copper or other metal with high conductivity, so as to avoid the introduction of resistance except where it is wanted. For the same reason all contact points must be kept clean and firmly screwed up. Care must be taken that nothing in the nature of a short circuit occurs through drops of water on the bench or on the resistance board. The changing over from the hydrogen cell to the standard cell is facilitated by a simple switchboard with holes containing mercury, into which the ends of the connecting wires are dipped. The ends of the wires must be well amalgamated to ensure good contact. Small potential differences may be measured in series with the standard cell, and a second reading taken with the two cells in opposition. The difference between the two readings, divided by two, gives the reading due to the experimental cell alone.

The actual cost of the apparatus, apart from the accumulator, is not great. It will naturally depend to a great extent on the technical resources of the laboratory, but in most cases £2 to £3 should cover it all. Where facilities exist for glass-blowing and for simple wood and metal working it could be made for much less. The inch or two of platinum wire required for the hydrogen electrode and for the contacts of the standard cell, the electrometer, and the calomel electrode will cost at most a few shillings.

APPLICATION OF THE METHOD.—As an instance of the application of this method to analytical problems, the results given below are of interest. They were obtained during an investigation of the action of various foodstuffs when cooked under practical conditions in lead-glazed earthenware casseroles (*cf.* H. Masters, ANALYST, 1919, **44**, 164).

| Nature of Food Cooked. | E.M.F. against $\frac{N}{10}$ Calomel Electrode. | H-Ion Concentration $P_H^+$. | Ratio of Lead dissolved per Unit of Surface to that dissolved subsequently from same Vessel by Heating to approximately 95° C. for Two Hours with 1 per cent. Citric Acid. |
|---|---|---|---|
| | Volts. | | |
| Rice, tomato, and onion ... | 0·649 | 5·40 | 0·064 |
| Beans, cabbage, potato, turnip, and onion ... | 0·647 | 5·36 | 0·043 |
| Steak, kidney, and onion ... | 0·676 | 5·86 | 0·217 |
| Rhubarb ... ... ... | 0·495 | 2·73 | 0·209 |
| One per cent. citric acid ... | 0·467 | 2·22 | 1·0 |

LIMITATIONS OF THE METHOD.—The course of a typical electrometric titration is shown in Fig. 4, which represents the titration of a dilute solution of hydrochloric acid with $\frac{N}{10}$ sodium hydroxide solution. The point of absolute neutrality is that at which the curve is steepest—*i.e.*, at which the hydrogen ion concentration changes most rapidly with successive additions of sodium hydroxide. In this particular case neutrality was reached with 11·3 c.c. of $\frac{N}{10}$ sodium hydroxide solution. It can be seen from this figure that in strongly acid or alkaline solutions

the change in hydrogen ion concentration is relatively small for a given change in the "titration acidity" of a solution. As we approach the neutrality point, the rate of change in hydrogen ion concentration becomes relatively much greater. The method is therefore not well adapted to the measurement of high acidities, and its main value lies in its power of differentiating between slight variations in reaction in the neighbourhood of the neutrality point. The subject of electrometric

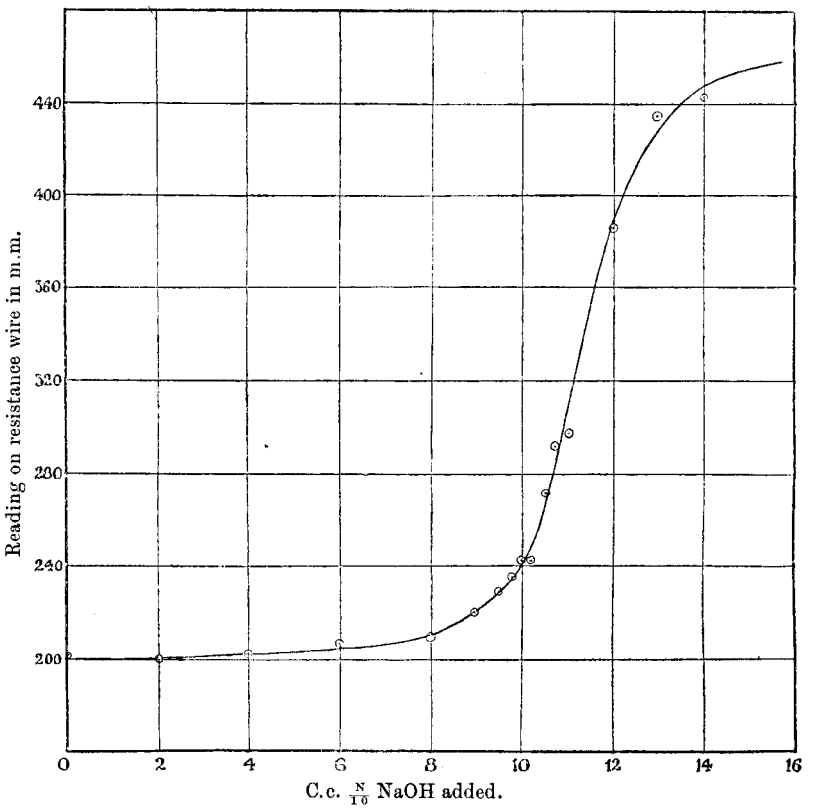


FIG. 4.—TYPICAL ELECTROMETRIC TITRATION.

titration as applied more especially to tan liquors was investigated by H. J. S. Sand, D. J. Law, and J. T. Wood (ANALYST, 1911, **36**, 121, 515), who described a special form of hydrogen electrode for this purpose.

My thanks are due to my assistant, Mr. W. A. Godby, for preparing the drawings given in this paper.

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# A FURTHER CONTRIBUTION TO THE STUDY OF SOUTH AMERICAN OILSEEDS.

By G. T. BRAY, A.I.C., and H. T. ISLIP, A.I.C.

During recent years considerable attention has been given to South America as a possible source of commercial supplies of oilseeds yielding oils and fats of technical importance. A large number of oilseeds from that country have been examined from time to time at the Imperial Institute, and the results of some of these investigations have already been published (*cf. Bull. Imp. Inst.*, 1917, **15**, 479; 1919, **17**, 186; 1920, **18**, 168, 172; Bray and Elliott, Analyst, 1916, **41**, 298), whilst papers on this same subject by other authors have also appeared in the Analyst (Bolton and Hewer, 1917, **42**, 35; Bolton and Revis, 1918, **43**, 251).

In this paper an account is given of the results of examination of four further varieties of South American oilseeds.

"Cupu" Seeds.—These seeds are derived from *Theobroma grandiflorum* (N.O. *Sterculiaceæ*), a tree which occurs in the district of the Upper Amazon and in the province of Para. The seeds are flat and roughly ovate, with a slight odour resembling that of cocoa. They consist of a thin, brittle, closely adhering, reddish-brown husk, covering a moderately soft, pale brown, oleaginous interior. The average dimensions of the seeds received at the Imperial Institute were 1·0 inch long, 0·8 inch broad and 0·25 inch thick, whilst the average weight of a seed was 2·2 grms.

The fat extracted with petroleum spirit was creamy white, of rather soft consistence, and practically devoid of taste or odour. From the chemical examination it would appear that this fat resembles cacao butter. Cupu fat, however, is softer than cacao butter, and lacks its brittleness and odour. It could probably be used for edible purposes.

The residual meal contained 1·0 per cent. of an alkaloidal body which gave the murexide reaction and was probably theobromine. This amount of alkaloid corresponds to 0·5 per cent. on the original seeds.

Hymenæa Fruits.—These fruits are derived from a species of *Hymenæa* probably *H. Courbaril* (N.O. *Leguminosæ*), which is found in South America and in Jamaica. The sample examined at the Imperial Institute consisted of large brown, rough, shiny pods about 5·7 inches long, 2·3 inches broad, and 1·2 inches thick. The pod-cases were about 0·2 inch thick, and were very hard and brittle. The pods contained on an average seven seeds embedded, generally together with a few small lumps of pale yellow resin, in a pale reddish-brown, soft, mealy material, which clung tenaciously to them. The seeds were of flattened oval shape, and had a very hard, tough, smooth, chocolate-coloured seed coat. The kernels were very hard, and of a pale cream colour internally. The average weight of a seed was 3 grms. The pods consisted of: Pod-cases, 74 per cent.; mealy material and resin, 6 per cent.; and seeds, 20 per cent.

The oil extracted from the seeds with petroleum spirit was nearly colourless, and had rather an unpleasant odour. Owing to the small amount of material available, the constants of the oil were not determined.

The residual meal was pinkish-brown and possessed a pleasant agreeable taste, but was found to be rather poor in protein. The mealy substance surrounding the seed is palatable, and is stated to be eaten by the natives of the West Indies.

PARINARIUM SEEDS.—The fruits of several species of *Parinarium* are already known to be oleaginous. The seeds of *P. Mobola* have been imported as an oilseed into Europe under the name of "Mabo" seeds, whilst the oil from *P. senegalense* seeds is occasionally used in Senegal for soap-making.

The present sample consisted of egg-shaped fruits with a reddish-brown, rough surface, marked by small irregular cracks. The dimensions of the fruits were from 2 to 3 inches long, and from 1·4 to 2·0 inches in diameter at the widest part. The shell, from 0·3 to 0·45 inch thick, was very tough and fibrous, and not easily removed from the kernel. The kernels were yellow and oily, but of firm consistence, and split easily, disclosing a long central cavity. They were covered with a light greyish-brown inner fibrous skin and a reddish-brown outer skin, both of which were readily detachable. The odour of the kernels was characteristic and unpleasant. The fruits were composed of 79 per cent. of shell and 21 per cent. of kernels. The average weight of a fruit was 29·3 grms. and of a kernel 7·6 grms.

The oil extracted with petroleum spirit was a thick, viscid, dark-brown oil, which on keeping became a soft semi-solid fat. It had a strong unpleasant odour. This oil differs considerably from a sample of "Po-yoak" oil from Sierra Leone examined at the Imperial Institute (*Bull Imp. Inst.*, 1918, **16**, 38), which is probably derived from the nuts of another species of *Parinarium*. The latter had drying properties, and polymerised to a solid mass on heating to 300° C. for twenty minutes in an oil-bath. The "Po-yoak" seeds are more globular and have a thinner shell than this South American variety.

The residual meal had an unpleasant bitter taste.

PLATONIA SEEDS.—These seeds were derived from a species of *Platonia* (N.O. *Guttiferæ*). They were somewhat irregular in shape, but their predominating form was a flattened ovoid, slightly concave on one side, their average dimensions being 2 inches long, 1 inch broad and $\frac{3}{4}$ inch thick. These seeds had a thin, closely adhering, tough brown skin, enclosing a firm oleaginous kernel, which varied in colour from greyish-white to brown, but in many seeds was brown throughout. The flesh in places showed minute cavities containing brown resinous material. The average weight of a seed was 11·8 grms.

The oil extracted with petroleum spirit was a dark-brown solid fat of fairly firm consistence, and having a slight aromatic odour.

The residue from the extraction with petroleum spirit yielded, on extraction with acetone, 3 or 4 per cent. of a soft brown resinous material. The residual meal was free from alkaloids and cyanogenetic glucosides.

The following table gives the results obtained in the examination of these seeds and the oils extracted from them :

| | *Theobroma grandiflorum* Seeds. | *Hymenæa Courbaril* Seeds. | *Parinarium* Species Kernels. | | *Platonia* Species Seeds. |
|---|---|---|---|---|---|
| | | | South America. | Sierra Leone. | |
| *Composition:* | | | | | |
| Moisture, per cent. ... ... ... | 8·2 | 11·5 | 3·4 | 8·7 | 3·2 |
| Oil on material as received, per cent. | 48·7 | 6·4 | 74·2 | 58·3 | 75·0 |
| Oil on material dried at 100° C., per cent. ... ... ... ... | 53·0 | 7·2 | 76·8 | 63·8 | 77·5 |
| *Analytical Values of Oil:* | | | | | |
| Melting-point, ° C.* ... ... ... | 32·0 | — | — | — | 31·0 |
| "Titre" of fatty acids, ° C. ... ... | 48·1 | — | 41·6 | 48·3 | 50·1 |
| Specific gravity ... ... ... | 0·8522† | — | 0·905† | 0·969‡ | 0·8782† |
| Acid value ... ... ... ... | 44·0 | — | 16·2 | 17·4 | 46·4 |
| Saponification value ... ... ... | 187·8 | — | 200·5 | 192·3 | 199·5 |
| Iodine value (Hübl, 17 hours), per cent. ... ... ... ... | 44·8 | — | 77·3 | 157·1 | 77·8 |
| Unsaponifiable matter, per cent. ... | 0·91 | — | 0·76 | 0·7 | 3·63 |
| Volatile acids, soluble§ ... ... | 0·08 | — | 2·68 | 0·2 | 0·13 |
| Volatile acids, insoluble§ ... ... | 0·12 | — | 0·52 | 0·4 | 0·37 |
| Refractive index $[n]_D^{40}$ ... ... | 1·456 | — | 1·469 | — | 1·469 |
| *Composition of Residual Meal:* | | | | | |
| Moisture, per cent. ... ... ... | 9·9 | 11·0 | 7·4 | 12·2 | 9·2 |
| Crude proteins, per cent. ... ... | 18·7 | 7·1 | 24·7 | 12·1 | 14·3 |
| Fat, per cent. ... ... ... ... | 7·0 | 7·0 | 7.0 | 7·0 | 7·0 |
| Carbohydrates, etc. (by difference), per cent. ... ... ... ... | 43·8 | 67·7 | 46·6 | 56·1 | 46·2 |
| Crude fibre, per cent. ... ... | 14·3 | 5·5 | 8·2 | 8·9 | 13·4 |
| Ash, per cent. ... ... ... | 6·3 | 1·7 | 6·1 | 3·7 | 9·9 |
| Nutrient ratio ... ... ... | 1 : 3·2 | 1 : 11·8 | 1 : 2·5 | 1 : 6·0 | 1 : 4·4 |
| Food units ... ... ... ... | 108 | 103 | 126 | 104 | 99 |

* Open tube method. † At 100°/15° C. ‡ At 15°/15° C.

§ C.c. of $\frac{N}{10}$ potassium hydroxide solution required to neutralise the volatile acids from 5 grms. of the oil.

CONCLUSIONS.—Of the four oilseeds described, "Cupu" (*Theobroma grandiflorum*) is the only one which can be considered as at all promising from a commercial point of view. The quantity of these seeds available is not known, so that it is not possible to state whether they can be exported in sufficiently large consignments to be of economic value.

The authors desire to express their thanks to Mr. T. B. Woodward, of Liverpool, for kindly supplying the seeds for examination.

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## NOTES.

*The Editor desires 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.*

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A SAMPLE marked "Chilian honey" was submitted for my opinion as to the risk of its sale as honey under the Food and Drugs Acts, even with the reservation of the word "Chilian."

The analysis as made by my chief assistant, Dr. H. E. Cox, F.I.C., M.Sc., was: Water, 21·50; ash, 2·0; cane sugar, 16·50; glucose, 4·0; raffinose, dextrin, proteins, traces; and invert sugar, 56·0. Total, 100·0.

In view of genuine honey giving, say, 75 per cent. of invert sugar with 20 per cent. of water, and about 5 per cent. cane sugar, dextrin, etc., I gave the opinion that the excess of cane sugar alone would preclude the sample being considered pure and unsophisticated honey.

What exactly "Chilian honey" may be is unknown to me; but if the above was genuine, the habits of the bees of Chili might repay investigation!

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## REPORTS OF PUBLIC ANALYSTS.

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

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# ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

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## FOOD AND DRUGS ANALYSIS.

**Mineral Constituents of Potatoes and Potato Flour. C. E. Mangels.** (*J. Ind. Eng. Chem.*, 1921, **13**, 418-419.)—Four samples of potatoes from different sources yielded the following results: Total ash, 4·31 to 5·70; calcium oxide, trace to 0·161; magnesium oxide, 0·236 to 0·290; potassium oxide, 2·12 to 2·69; phosphoric anhydride, 0·685 to 0·730; sulphur, 0·108 to 0·164; and chlorine, 0·076 to 0·260 per cent. The flours prepared from these potatoes contained: Total ash, 3·51 to 4·90; calcium oxide, trace to 0·145; magnesium oxide, 0·198 to 0·279; potassium oxide, 1·82 to 2·51; phosphoric anhydride, 0·438 to 0·655; sulphur, 0·105 to 0·155; and chlorine, 0·066 to 0·197 per cent. All these results are expressed as percentages of the dry substance. The relative distribution of the constituents of the ash is not altered appreciably during the process of manufacture of the flour; bolted flour made

from peeled potatoes has practically the same composition as unbolted flour made from unpeeled potatoes, but the former has a better colour. W. P. S.

**Carbohydrate Content of the Navy Bean and Peas. W. H. Peterson and H. Churchill.** (*J. Amer. Chem. Soc.*, 1921, **43**, 1180-1185.)—Analyses made by the methods of the Association of Official Agricultural Chemists of navy beans, Alaska garden peas, and Canada field peas, showed the nitrogen-free extracts to amount to 58·97—61·80, 60·26 and 54·47 per cent., whilst the starch present was 35·20—50·54, 51·21, and 45·11 per cent. respectively. Extremely fine grinding of the material is essential for the complete digestion of the starch by diastase solution, an ordinary feed-mill grinding yielding from 10 to 12 per cent. less starch. The blue colour given on the addition of iodine is too sensitive to indicate when the whole of the starch is saccharified, and other substances present may also show this reaction. A digestion for four hours with malt extract is probably sufficient to convert the starch completely enough for analytical purposes. Tables showing the kind and amount of carbohydrates contained in the various extracts, the complete analysis of navy beans, and the effect of varying digestion periods upon the estimation of starch by diastase are given. T. J. W.

**Structure of Foreign Haricot Beans. N. T. Giung.** (*Comptes rend.*, 1921, **172**, 1436-1438.)—The small haricots cultivated in tropical countries are usually grouped under the name of *Phaseolus Mungo* (L.), although they include three distinct species, *P. Mungo*, *P. radiatus* (Roxb.), and *P. aureus* (Roxb.). The various species of *Phaseolus* may be differentiated by the structure in their seminal teguments, which, in the case of *P. Mungo* and *P. aureus*, are composed of three layers, as compared with five in the case of *P. vulgaris* and *P. multiflorus*. On the other hand, the teguments of certain other species such as *P. calcaratus* have also three layers, but show a very different sub-epidermic structure. The tegument of *P. Mungo* has (1) an epidermic layer, composed of cells the cavity of which contains a green substance, and is club-shaped; (2) a sub-epidermic layer, the cells of which (also containing a green substance) are shaped like dumb-bells, and show regular hexagonal openings between them; and (3) a parenchyme composed of cells with thin walls ranged tangentially, those of the last layers being very flattened. In the case of *P. aureus* the cells of the sub-epidermic layer are less regular in form, and the passages between the cells are irregularly oval, instead of hexagonal, and are also less constantly present. As a rule, the seeds of *P. Mungo* have a blackish-green tegument, more or less covered with yellow-orange spots, and have a somewhat prominent hilum, whilst those of *P. aureus* have a more uniformly green tegument and a hilum which is, at most, only slightly prominent. The *green haricot* of Indo-China agrees in morphological characteristics with *P. aureus*.

**Amylases of the Cereal Grains—Rye. J. L. Baker and H. F. E. Hulton.** (*J. Chem. Soc.*, 1921, **119**, 805-809.)—Potato starch paste is rapidly liquefied by ungerminated rye diastase at 50° C., and the conversion products are easily separated by precipitation with alcohol. About 22 per cent. of the original starch is obtained

as a dextrin, having the constants $R_{3\cdot93}$ 1·5 and $[\alpha]_{D3\cdot93} = 184\cdot1°$, the only other product yielded being maltose, which was readily crystallised out in a state of purity after evaporation of the alcoholic solution. The dextrin, on degradation for twelve hours at 50° C. with rye amylase, and also with malt amylase, yielded products of similar character to those obtained by the enzymes of ungerminated and germinated barley upon *a*-amylodextrin previously described by one of the authors (*J. Chem. Soc.*, 1902, **77**, 1177). Repeated precipitation by alcohol of the dextrin produced by rye amylase caused no change in the rotatory or reducing powers, and this substance is, therefore, probably identical with the previously described *a*-amylodextrin. The amylase of germinated rye, under the above conditions, yields crystalline maltose and an unfermentable reducing dextrin having R = 10·8 and $[\alpha]_D = 181\cdot9°$. No intermediate malto-dextrins are produced, and practically the whole of the apparent maltose is fermentable by yeast. T. J. W.

**Influence of Ammonium Molybdate on the Rotatory Powers of Certain Sugars. G. Tanret.** (*Comptes rend.*, 1921, **172**, 1363-1365.)—As previous authors have observed, the presence of ammonium molybdate produces a considerable change in the specific rotation of pentoses and hexoses, whereas hydrolysable sugars and cyclic compounds such as quercitol and *l*-inositol are not affected in this way. It is suggested that the effect produced by the molybdate may be utilised as a means for estimating certain sugars by isolating the complexes in crystallisable form.

T. H. P.

**Influence of Ammonium Molybdate on the Rotatory Power of Mannitol. G. Tanret.** (*Comptes rend.*, 1921, **172**, 1500-1503.)—The slight lævo-rotation of mannitol is changed in sign by addition to the solution of ammonium hepta-molybdate, the dextro-rotation reaching a maximum when the relationship between the amounts of the two compounds corresponds with the formula:

$$[(13MoO_3, 7NH_3, 7C_6H_{14}O_6) - 6H_2O] + 3H_2O.$$

A well-defined complex compound of this composition is readily isolated by simple crystallisation. T. H. P.

**Table for the Estimation of Dextrose, Invert Sugar, and Lævulose by the Thiocyanate-Potassium Iodide Method. G. Bruhns.** (*Chem. Zeit.*, 1921, **45**, 486-487.)—The method is as follows: Ten c.c. of copper sulphate solution (69·5 grms. per litre), 10 c.c. of alkaline tartrate solution (346 grms. of Rochelle salt and 100 grms. of sodium hydroxide per litre), 10 c.c. of sugar solution (containing not more than 0·9 per cent. of sugar), and 10 c.c. of water are mixed, heated to boiling, and boiled for exactly two minutes; 50 c.c. of cold water are then added, the mixture is cooled rapidly, 5 c.c. of potassium thiocyanate-iodide solution (65 grms. of potassium thiocyanate and 10 grms. of potassium iodide per 500 c.c.) and 10 c.c. of 6*N* hydrochloric acid are introduced, and the mixture is at once titrated with thiosulphate solution (34·4 grms. of the salt and 2 c.c. of *N*/1 sodium hydroxide solution per litre; the strength of this solution is 0·1387*N*), starch solution being added as indicator towards the end of the titration. A similar mixture, containing the same quantities of

the reagents without the sugar solution, is titrated at the same time. The difference between the two titrations, in terms of c.c. of thiosulphate solution, is a measure of the sugar present, the quantity of the latter being found by reference to a table. The following values are taken from the full table given in the original:

| Thiosulphate Solution. | Dextrose. | Invert Sugar. | Lævulose. |
|---|---|---|---|
| C.c. | Mgrms. | Mgrms. | Mgrms. |
| 0·1 | 0·45 | 0·45 | 0·45 |
| 0·5 | 2·20 | 2·30 | 2·35 |
| 1·0 | 4·40 | 4·60 | 4·70 |
| 1·5 | 6·60 | 6·90 | 7·10 |
| 2·0 | 8·80 | 9·20 | 9·45 |
| 2·5 | 11·05 | 11·50 | 11·95 |
| 3·0 | 13·25 | 13·80 | 14·40 |
| 4·0 | 17·65 | 18·45 | 19·25 |
| 5·0 | 22·15 | 23·15 | 24·10 |
| 6·0 | 26·70 | 27·85 | 29·05 |
| 7·0 | 31·30 | 32·65 | 34·05 |
| 8·0 | 35·95 | 37·45 | 39·10 |
| 9·0 | 40·70 | 42·35 | 44·20 |
| 10·0 | 45·50 | 47·35 | 49·30 |
| 11·0 | 50·35 | 52·35 | 54·50 |
| 12·0 | 55·30 | 57·45 | 59·75 |
| 13·0 | 60·30 | 62·00 | 65·05 |
| 14·0 | 65·40 | 67·85 | 70·40 |
| 15·0 | 70·60 | 73·15 | 75·80 |
| 16·0 | 75·85 | 78·55 | 81·30 |
| 17·0 | 81·20 | 84·00 | 86·85 |
| 18·0 | 86·70 | 89·53 | 92·45 |
| 19·0 | 92·25 | 95·15 | 98·10 |

W. P. S.

**Composition of Grape-Seed Oil. E. André.** (*Comptes rend.*, 1921, **172**, 1413-1415.)—The high figures recorded for the acetyl value of grape-seed oil (13·3 to 144·5) have been attributed, though without sufficient proof, to the presence of ricinoleic acid. Hydroxy fatty acids could not be isolated from a sample of the oil by any of the usual methods of analysis, these only indicating the presence of palmitic, stearic, oleic, and linolic acids, but by fractional crystallisation of the lithium salts from dilute alcohol the hydroxy acids were separated from the solid and liquid acids. The mixed fatty acids (freed from unsaponifiable matter) from 125 grms. of grape-seed oil (acetyl value, 49·3) were dissolved in 3 litres of 70 per cent. alcohol, and the solution boiled for an hour with 40 grms. of lithium carbonate beneath a reflux condenser, and then left in a cold place for twenty-four hours. The first crystals consisted mainly of the lithium salts of solid fatty acids (iodine value, 32); the solution was concentrated by distillation, and then yielded crystals of lithium salts of the liquid fatty acids (iodine value, 131); whilst the mother liquor contained the lithium salts of the hydroxy fatty acids. When isolated, these

were of viscous consistence, and had iodine value 110 and molecular equivalent 277. The average yields from the mixed fatty acids were: Solid acids, 12·5; liquid acids, 62·5; and viscous acids, 25·0 per cent. The low molecular equivalent of the hydroxy fatty acids did not support the view that they consisted of ricinoleic acid.

**Estimation of Glycerol in Wine by Conversion into Acrolein. A. Heiduschka and F. Englert.** (*Zeitsch. anal. Chem.*, 1921, **60**, 161-166.)—A method is described for estimating glycerol in wine based on its conversion into acrolein by boric acid, as suggested by Wohl and Neuberg (*Ber.*, 1899, **32**, 1352). The extract from 100 c.c. of wine is mixed with 15 c.c. of water, and evaporated to 2 to 3 c.c. in a quartz retort heated on a bath of melted alloy. One grm. of boric acid is added, and the mixture heated until evolution of steam ceases. The retort is then connected with two Péligot tubes immersed in a freezing mixture and containing 20 c.c. of 25 per cent. ammonia; a tube from an air reservoir is passed through the tubulure of the retort. The bath is gradually heated to 320° C., formation of acrolein commencing at 250° C.; a current of air is then slowly passed through the vessel, and heating is continued for forty-five minutes. The contents of the Péligot tubes are then treated with 5 c.c. of $\frac{N}{10}$ silver nitrate solution and warmed until a faint ammoniacal reaction persists. The precipitated silver is filtered off through glass-wool, the filtrate is treated with 5 c.c. of saturated ferric ammonium sulphate solution and dilute nitric acid until decolorised, and the silver is estimated with $\frac{N}{10}$ ammonium thiocyanate. The amount of glycerol may then be found by the aid of a table giving the amount of silver nitrate reduced by pure glycerol. The results by this method are lower than those obtained by the lime and iodide methods and are more nearly in agreement with the theoretical. They are not affected by any substances present in wine, or by other aldehydes, such as croton aldehyde, formed by the action of boric acid. W. J. W.

**Polarimetric Estimation of Tannin in Hops. A. R. Ling and D. R. Nanji.** (*J. Inst. Br.*, 1921, **27**, 310-313.)—The following method is based upon previous work by Chapman (ANALYST, 1907, **13**, 646), which indicated that 1 grm. of cinchonine is precipitated by 1·217 grms. of hop tannin. Ten grms. of hops are weighed out and extracted with water for two hours on a boiling water bath. After cooling, the mixture is diluted to 508 c.c., filtered, and 100 c.c. of the filtrate is evaporated to slightly less than half its volume, and 50 c.c. of standard cinchonine sulphate (approximately 1 per cent.) are added. The amount of cinchonine present in the clear solution is estimated by the optical rotation, using Landolt's figure of $[\alpha]_D$ 170·3°, and a similar reading is taken of the original cinchonine solution. From these readings, allowing for the dilution of the alkaloidal solution by the hop extract, the amount of cinchonine precipitated is calculated from which the quantity of hop tannin present is deduced. The results obtained are in good agreement with those given by Chapman's gravimetric method. T. J. W.

**The Turner Reaction for Gurjun Balsam. J. B. Luther.** (*J. Assoc. Off. Agric. Chem.*, 1921, **4**, 422-424.)—The method described in the U.S. Pharmacopœia

for the detection of gurjun balsam in copaiba (and known as the Turner reaction) has the disadvantage that the concentrated sulphuric acid is liable to char the mixture at the point of contact, and so obscure the coloration. This defect is eliminated by modifying the test as follows: Four drops of the oil are dissolved in 1 c.c. of glacial acetic acid, 1 drop of 10 per cent. sodium nitrite solution is added, and 2 c.c. of a 5 per cent. (by vol.) sulphuric acid solution in glacial acetic acid are then introduced and mixed quickly. A violet coloration indicates the presence of gurjun balsam. Colorations which develop after the lapse of ten seconds must be ignored.

W. P. S.

**New Lead Number Estimation in Vanilla Extracts. H. J. Wichmann.** (*J. Ind. Eng. Chem.*, 1921, **13**, 414-418.)—In the ordinary method of estimating the lead value of vanilla extracts the precipitation is not complete, being only that which occurs under an arbitrary set of conditions. To obtain a maximum precipitation and to save time, a method is described in which estimations of the lead value and alcohol content are combined. A mixture of 175 c.c. of water, 25 c.c. of 8 per cent. neutral lead acetate solution, and 50 c.c. of vanilla extract is distilled; 200 c.c. of distillate are collected, and the specific gravity of this distillate gives the alcohol content. The residue in the distillation flask is transferred to a 100 c.c. flask with water free from carbon dioxide, cooled, diluted to 100 c.c., and filtered. Ten c.c. of the filtrate are treated with 25 c.c. of water, 10 c.c. of dilute sulphuric acid, and 100 c.c. of 95 per cent. alcohol; the lead sulphate is collected, washed with alcohol, dried, ignited, and weighed. A control estimation is carried out at the same time, using water containing 5 drops of glacial acetic acid in place of the vanilla extract, and the number of grms. of lead precipitated by 100 c.c. of the extract is then calculated. The results obtained are about 34 per cent. higher than those found by the usual method; the lowest value obtained for an undiluted genuine vanilla extract was 0·55. The presence of sugar, glycerol, and coumarin does not affect the accuracy of the method, but the method must be modified as follows if added vanillin is present in the extract: Fifty c.c. of the extract are shaken with 25 c.c. of ether; 25 c.c. of petroleum spirit are then added, and the mixture is again shaken; if, after standing, the mixture does not separate into a brown aqueous layer and a colourless ethereal layer, further small quantities of petroleum spirit are added. The aqueous layer is drawn off, and the ethereal solution washed with 2 c.c. of water. The extraction with ether and petroleum spirit is repeated, and the aqueous solution then used for the estimation of the lead value.

W. P. S.

**Essential Oil from Leaves of *Skimmia laureola*. J. L. Simonsen.** (*J. Soc. Chem. Ind.*, 1921, **40**, 126-127T.)—By distillation in steam at 25 lbs. pressure of the leaves of *Skimmia laureola*, 0·5 per cent. of an emerald green oil was obtained: Sp. gr. (30/30°), 0·9041; $[n]_D^{30}$, 1·4648; acid value, 3·63; saponification value, 197·96; saponification value after acetylation, 238·6. By prolonged fractional distillation of this oil under a pressure of 200 mm., the following fractions were isolated: (1) 130-140°, 0·46 per cent.; (2) 140-145°, 4·6 per cent.; (3) 145-150°, 0·61 per cent.;

(4) 150-155°, 8·4 per cent.; (5) 155-160°, 2·3 per cent.; (6) 160-167°, 2 per cent.; (7) 167-173°, 50 per cent.; (8) 173-177°, 0·61 per cent.; (9) 177-182°, 1·05 per cent.; (10) 182-190°, 1·2 per cent.; and (11) above 190°, 18·2 per cent. From fractions 1, 2, and 3, on redistillation, a considerable fraction was obtained which boiled at 130-135° (200 mm.) and at 176-182° (695 mm.). Analysis showed: C, 85·5; and H, 11·6 per cent. Its constants were: Sp. gr. (30/30°), 0·859; $[n]_D^{30}$, 1·471; and $[\alpha]_D^{30}$, −4·11. The nature of the hydrocarbon of which these fractions apparently consist was not definitely determined. Fraction 4 consisted of nearly pure *l*-linalool, and fractions 5 and 6 were mixtures of *l*-linalool and *l*-linalyl acetate. The bulk of the oil which was obtained in fraction 7 consisted of pure *l*-linalyl acetate; its constants were: Sp. gr. (30/30°), 0·892; $[n]_D^{30}$, 1·4537; and $[\alpha]_D^{30}$, −7·25°. Fractions 8 and 9 consisted chiefly of linalyl acetate; the latter showed traces of a high-boiling alcohol after hydrolysis; this was also the case with fraction 10. No fraction of constant b.-pt. could be obtained from fraction 11. The carbon content of the various fractions varied from 76·1 to 81·0 per cent., and the hydrogen from 10·3 to 11·2 per cent. Those fractions distilling above 175° varied in colour from emerald green to indigo blue, and the higher boiling fractions showed a blue fluorescence, but methyl anthranilate was absent. W. J. W.

**Volatilisation of Ethyl Nitrite from Sweet Spirit of Nitre. J. G. Roberts.** (*Amer. J. Pharm.*, 1921, **93**, 320-324.)—Experiments are described designed to determine the influence of the various factors concerned in the storage and dispensing of sweet spirit of nitre, which lead to the loss of ethyl nitrite. The results obtained clearly show that the chief loss is due to evaporation, which may arise from agitation and exposure to air, the frequent sampling from a large bottle, and the storage of small amounts of the drug in large bottles. Direct sunlight also causes a rapid decomposition of the ethyl nitrite when small white flint glass bottles are completely filled with spirit of nitre, but in similar bottles of amber glass a loss of only 0·06 per cent. occurs under the same conditions during four weeks. Practically the whole of the ethyl nitrite present is lost on exposure in a porcelain basin at the ordinary temperature in $1\frac{1}{2}$ hours. The ideal method of storing sweet spirit of nitre is in small completely filled bottles of amber glass kept in a refrigerator, when no appreciable loss of ethyl nitrite will occur in a month. T. J. W.

**Microchemical Identification of Hydrocyanic Acid by Means of Alloxan Reagent. G. Deniges.** (*Ann. Chim. Anal.*, 1921, **3**, 179-182.)—In the presence of minute traces of hydrocyanic acid, characteristic crystals are produced by the interaction of ammonia and alloxan, the hydrocyanic acid acting as a catalyst only. The alloxan reagent is prepared as follows: Two grms. of uric acid are treated with 2 c.c. of nitric acid (sp. gr. 1·38) until nitrous vapours cease to be evolved; 2 c.c. of water are then added, and the liquid heated until clear, and finally made to 100 c.c. For the detection of hydrocyanic acid, a drop of alloxan reagent is placed on a cover-slip, and a minute quantity of ammonia is added immediately; the cover-slip is then inverted over the mouth of a small test-tube

(about 18 × 50 mm.) containing the solution suspected to contain hydrocyanic acid, and allowed to remain for a short time. The test may also be carried out by exposing a drop of dilute ammonia in the same way, and then adding a minute quantity of the alloxan reagent; the substitution of pyridine for ammonia results in a still more sensitive reaction. The test is capable of indicating as little as $\frac{1}{10000}$ of 1 mgrm. of hydrocyanic acid. The mixture of alloxan reagent with pyridine or ammonia must be made immediately before use. The reaction can be used for the detection of hydrocyanic acid derived from cyanogenetic glucosides in beans, etc., by exposing a drop of the reagent for a few hours over the mouth of a test-tube containing a few grams of the material ground in water. R. G. P.

**Examination of Some Methods of Ascertaining the Purity of Saccharin. P. V. McKie.** (*J. Soc. Chem. Ind.*, 1921, **40**, 150-152T.)—Pure saccharin melts at 227° to 227·5° C. (corr.); study of the melting-point curves of mixtures of saccharin *o*- and *p*-sulphamidobenzoic acids and with *o*-toluenesulphonamide shows that the melting-point is a safe guide to the percentage composition of mixtures up to 10 per cent. in the case of the para-acid (m.-pt., 288° to 289° corr.) and the ortho-amide. Mixtures with the ortho-acid cannot be estimated by the melting-point, as this acid decomposes at 180° C. If a 6 to 8 per cent. solution of sodium bicarbonate be added to the powdered saccharin until effervescence ceases, and the mixture filtered after standing, *o*- and *p*-toluenesulphonamides and toluene-2·4-disulphonamide are left behind, and pure saccharin can be precipitated from the filtrate by adding 30 to 50 per cent. excess of 5 per cent. hydrochloric acid at 80° C. When saccharin is estimated by the usual method of hydrolysing with acid and distilling the ammonia, *o* and *p*-toluenesulphonamide and toluene-2·4-disulphonamide are not hydrolysed, and so do not interfere with the accuracy of the method, but *o*-sulphamidobenzoic acid is largely hydrolysed, so that this not very common impurity introduces considerable inaccuracy in the estimation (*cf.* ANALYST, 1919, **44**, 99). H. E. C.

## BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

**Investigations on the Rancidity of Butter and Margarine Fats. W. N. Stokoe.** (*J. Soc. Chem. Ind.*, 1921, **40**, 75-81T.)—The rancidity of butter and margarine is almost wholly caused by the action of micro-organisms; the first stage appears to be hydrolysis, and this is followed by oxidation and a number of other reactions. The kinds or forms of rancidity are several, and may be classified according to the appearance, odour, and taste of the fat. Oxidation and heat produce a stale greasy taste in the fat; the tallowiness of old butter is another instance of this form of rancidity. Another kind of rancidity is that in which the fat acquires an aromatic odour and a most objectionable pungent taste; this may occur in margarine only a few days old. Investigation showed that mould organisms, principally *Penicillium* species, were present in these rancid margarines, and that the growth of *Penicillium* or of *Aspergillus* on media containing coconut oil or palm-kernel oil produced this form of rancidity; the effect appears to be brought about by an enzyme secreted by the mould acting probably in conjunction with the lipase secreted by the

same organism. The substance produced and giving rise to the odour and taste is a ketone or mixture of ketones (principally methyl-nonyl-ketone); aldehydes are not present. In cases of rancidity where there is a marked discoloration of the butter or margarine, the effect is produced by moulds and also by bacteria and yeasts; the following organisms were isolated from rancid butter and margarine: *B. fluorescens liq.*, *B. proteus* species, *B. coli*, *B. putrificus*, *B. punctatum*, *M. luteus*, *S. lutea*, wild yeasts, torulæ, etc. Yeast organisms are found frequently in butter, and their action may be capable of useful development; if a mixture of fats containing coconut oil be inoculated with yeast, a faint, slightly fruity odour is produced. Certain acid-resisting yeasts appear to have the property of associating themselves with the lactic acid organisms, whereby the life of the latter is prolonged.

W. P. S.

**Black Spot of Citrus Fruits. H. A. Lee.** (*Philippine J. Science*, 1920, **17**, 635-641.)—The black spots formed on the rind of oranges, lemons, mandarins, and other citrus fruits, are due to a fungus, *Phoma citricarpa*, which develops in storage and is especially found on oranges grown in China. The fungus may be cultivated on beef agar, glucose agar, or potato, but is frequently overgrown by secondary fungi. The diagnostic features are the black, carbonaceous, restricted growth on culture, and the thin-walled, granular, characteristic spores (9·25 to 12·25 × 5·5 to 8·1 $\mu$). The fungus should produce a growth on sweet oranges in fifteen to twenty days. The disease is common in Australia, but is not yet known in the orchards of America or Japan.

**Sudden Physiological Mutations caused by Individual Divergences of Lactic Organisms. C. Gorini.** (*Comptes rend.*, 1921, **172**, 1382-1384.)—Normally lactico-proteolytic organisms first coagulate milk and then dissolve the coagulum, but occasionally a variety is encountered which peptonises milk without previously coagulating it. This modification, which exhibits diminished acidifying power, transmits its properties, although cases of retromutation—that is, reversion after several generations to the original behaviour—have been observed. It is suggested that the organism contains some cells in which the saccharolytic, and others in which the proteolytic, power predominates, and that the prevalence of the one or the other type in the seeding determines the character of the resulting culture. T. H. P.

**Diagnosis of Individual Blood and Sperm. Dervieux.** (*Comptes rend.*, 1921, **172**, 1384-1386.)—Five doses of one and the same human sperm containing living spermatozoa were administered subcutaneously to a rabbit at intervals of three days. After the lapse of three weeks blood was withdrawn from the carotid of the rabbit, the serum being collected aseptically and stored in sealed tubes. The behaviour of the serum towards human sperm, male and female human blood, and the blood and sperm of the individual supplying the sperm injected into the rabbit, was investigated, the results obtained showing that it is possible in this way (1) to ascertain if a sperm is of human origin and from which particular individual it was derived, and (2) to determine if any sample of blood is of human origin, to diagnose it as male or female blood, and to ascertain if it is or is not the blood of a

particular individual. If the sperm of different animals be employed, the method may possibly be applied more generally. T. H. P.

## WATER ANALYSIS.

**Soap Solution for Use in Estimating Hardness of Water. A. Krieger.** (*Chem. Zeit.*, 1921, **45**, 559-560.)—The author recommends the use of a 10 *N* soap solution instead of normal Clark's solution; it is prepared by dissolving 20 grms. of potash soap in 50 c.c. water, and adding 94 per cent. alcohol up to 700 c.c. An appreciable saving of alcohol is effected. W. J. W.

**Estimation of the Hardness of Water. G. Brühns.** (*Zeitsch. angew. Chem.*, 1921, **34**, 279.)—Winkler's method (*Zeitsch. angew. Chem.*, 1921, **34**, 115) has been slightly modified: 150 c.c. of the sample are treated with $\frac{N}{10}$ hydrochloric acid, with methyl orange as indicator, until a red coloration persists and free carbon dioxide is expelled. About 0·03 to 0·05 grm. of precipitated calcium carbonate is added, and then 25, 50, or 75 c.c. of Wartha's solution, dependent on the degree of hardness, after which the solution is diluted to 250 c.c. After remaining for half to one hour until two-thirds of the solution have settled clear, a sample is withdrawn and tested for alkalinity. W. J. W.

**Detection of Phenols in Water. R. D. Scott.** (*J. Ind. Eng. Chem.*, 1921, **13**, 422.)—The reagent used is that proposed originally by Folin and Denis for the colorimetric estimation of phenols in urine; it is prepared by boiling a mixture of 750 c.c. of water, 100 grms. of sodium tungstate, 18 grms. of molybdic acid, and 50 c.c. of 85 per cent. phosphoric acid for two hours under a reflux condenser. The solution is then cooled and diluted to 1 litre. Five hundred c.c. of the water to be tested are acidified with 10 c.c. of sulphuric acid (1 : 1) and distilled; 100 c.c. of distillate are collected, and treated with 1 c.c. of the reagent and 5 c.c. of saturated sodium carbonate solution. The distillate from a water containing as little as 0·1 part per million of phenol gives a distinct blue coloration. The distillation removes substances (especially tannin) which interfere, and the test becomes practically specific for phenols. W. P. S.

**Detection of Fluorescein in very Dilute Solutions. M. Lombard.** (*Bull. Soc. Chim.*, 1921, **29**, 462-464.)—Fluorescein is commonly used as a powerful colouring matter in the investigation of the contamination of drinking-water. The identification of fluorescein in very dilute solutions may be effected by acidifying 30 c.c. of the water with a few drops of sulphuric acid or of hydrochloric acid (free from chlorine), and shaking with sufficient ether to yield a layer of 3 to 4 mm.; a few drops of ammonia are then added and mixed by gentle shaking, when, in the presence of fluorescein, the ether layer appears green when seen against a dark background; on standing, the fluorescein, which is more soluble in water than in ether, tinges the surface of the aqueous layer. One part of fluorescein in 200,000,000 may be detected. For greater dilutions, 200 c.c. of water are acidified and extracted with

30 c.c. of ether, the ether layer is then separated from most of the water, concentrated by evaporation, and examined after adding ammonia; $\frac{1}{1000000000}$ of fluorescein may be detected by this means. R. G. P.

## AGRICULTURAL ANALYSIS.

**Estimation of Urea in Fertilisers. E. B. Johnson.** (*J. Soc. Chem. Ind.*, 1921, **40**, 126T.)—For the estimation of urea, advantage is taken of the fact that it forms a slightly soluble salt with oxalic acid, the solubility of this salt being kept as low as possible by suitable precautions. Two to 5 grms. of the dried sample are extracted with 100 c.c. of anhydrous amyl alcohol, 25 to 50 c.c. of the filtrate treated with an equal volume of ether, and 25 c.c. of a 10 per cent. solution of anhydrous oxalic acid in amyl alcohol added. The precipitate is stirred and allowed to stand in cold water for thirty minutes, after which it is collected on a Gooch crucible, washed with a mixture of equal parts of amyl alcohol and ether, and then with ether alone, dried in a vacuum desiccator, and weighed. The necessary corrections for solubility are indicated by the following table :

| Urea found (grms.) : | 0·005 | 0·01 | 0·02 | 0·04 | 0·05 | 0·08 |
|---|---|---|---|---|---|---|
| Percentage of actual amount present : | 90·0 | 92·8 | 95·2 | 97·5 | 98·0 | 98·8 |

In cases where the urea is present in the fertiliser as a salt, or in complexes such as $Ca(NO_3)_2,4CO(NH_2)_2$, it will not dissolve completely in amyl alcohol and must therefore first be liberated. W. J. W.

## ORGANIC ANALYSIS.

**Iodimetric Estimation of Mercaptans. J. W. Kimball, R. L. Kramer, and E. E. Reid.** (*J. Amer. Chem. Soc.*, 1921, **43**, 1199-1200.)—About 0·25 grm. of the sample is weighed in a stoppered weighing bottle, and dropped into a bottle containing 35 c.c. of $\frac{N}{10}$ iodine in aqueous potassium iodide solution. The bottle is immediately stoppered and well shaken, and the excess of iodine titrated with $\frac{N}{10}$ sodium thiosulphate solution, starch being used as an indicator. A series of estimations made on various aliphatic mercaptans of approximate purity gave very uniform results with the same sample. T. J. W.

**Iodimetric Estimation of Acetone. P. H. Hermans.** (*Chem. Weekblad*, 1921, **18**, 348.)—The accuracy of the iodoform method for estimating acetone is dependent on the proportion of potassium hydroxide added to the aqueous acetone solution. Suitable amounts are: For 20 c.c. of acetone solution, 10 to 15 c.c. of $1\frac{1}{2}$ *N* KOH; and for 100 c.c. of acetone solution, 25 to 30 c.c. of $1\frac{1}{2}$ *N* KOH. In the first case the conversion into iodoform is complete in one to two minutes, and in the second case in three to five minutes. In an experiment with 0·2353 grm. of acetone in 100 c.c. water, 10 c.c. diluted to 100 c.c., and treated with 30 c.c. of potassium hydroxide solution and 25 c.c. of $\frac{N}{5}$ iodine solution, gave 99·9 per cent. acetone. In a second experiment, 10 c.c. were diluted to 20 c.c. and to 80 c.c. respectively, and 10 c.c. were distilled and diluted to 100 c.c.; the amounts of hydroxide added in the

three cases were 12, 25, and 30 c.c., and the iodine was added as before. After acidifying and titrating with thiosulphate, 99·5 per cent. of acetone was obtained in each case. W. J. W.

**Direct Estimation of Dicyanodiamide. E. B. Johnson.** (*J. Soc. Chem. Ind.*, 1921, **40**, 125-126T.)—A volumetric method for the estimation of dicyanodiamide is based on the precipitation of a compound of silver picrate with 2 mols. dicyanodiamide (*cf.* Harger, *J. Ind. Eng. Chem.*, 1920, **12**, 1107). Five grms. of the sample, or a correspondingly larger amount if the nitrogen be less than 5 to 15 per cent., are treated with 450 c.c. of cold water, glacial acetic acid being added to dissolve lime if present. The mixture is shaken for three hours, diluted to 500 c.c., and filtered. To 100 c.c. of the filtrate are added 5 c.c. of 20 per cent. nitric acid and 20 c.c. sodium picrate solution at 40° C.; the solution is then cooled to 5° C. and titrated with $\frac{N}{2\cdot2\cdot4}$ silver nitrate solution, of which about 2 c.c. are added in excess of that required by the amount of dicyanodiamide believed to be present. After vigorous shaking, the mixture is allowed to stand for fifteen minutes at 5° C., diluted to 200 c.c. with cold water, and filtered. Excess of silver solution is then titrated with $\frac{N}{2\cdot2\cdot4}$ sodium thiocyanate solution, after addition of 5 c.c. of 20 per cent. nitric acid and 2 c.c. of 5 per cent. ferric sulphate solution as indicator. With a 5 grm. sample, each c.c. of silver solution corresponds to 1 per cent. of nitrogen as dicyanodiamide. The results are affected by the excess of silver solution or the amount of nitric acid used, whilst temperature has also an influence on the precipitation. Suitable corrections must therefore be worked out, but none is necessary in the case of calcium cyanamide if 5 c.c. of 20 per cent. nitric acid per grm. of calcium acetate be used, together with an excess of 2 c.c. of silver nitrate. The method is not affected by the presence of urea and dicyanodiamidine; if chlorides and soluble sulphides be present, a blank titration of the silver solution without addition of picric acid must be made. The results agree closely with those obtained by the modified Caro method. W. J. W.

**Estimation of Fatty Acids in Turkey-Red Oil.** (*Chem. Zeit.*, 1921, **45**, 560-561.)—For the volumetric estimation of the fatty acids in Turkey-red oil, 10 to 20 grms. of the sample are heated with 25 c.c. of water until dissolved. The solution is transferred to a Büchner flask, 30 c.c. of concentrated hydrochloric acid are added, and the mixture is heated for twenty minutes over the naked flame. Sufficient concentrated solution of sodium chloride at 100° C. is then added to cause the fatty acid layer to enter the tube of the apparatus, and, after fifteen minutes on the water-bath, the volume of fatty acids is read off, the percentage by weight being calculated by means of a specific gravity determination. For the gravimetric estimation, 10 grms. of the sample are dissolved in 50 c.c. water in a porcelain crucible on a water-bath, 15 c.c. concentrated hydrochloric acid are added, and the mixture is left for thirty minutes, during which period the layer of fatty acids is agitated with the acid liquid. When the fatty acids have separated clearly, 10 grms. of wax are added, and the mixture is allowed to remain on the water-bath for thirty minutes with agitation, after which it is left to settle for an equal period, and cooled. The wax is then re-

moved, rinsed, melted in distilled water, solidified and dried, heated in a crucible for thirty minutes at 105° to 110° C., and weighed. The weight of fatty acids is then calculated. W. J. W.

**Estimation of Resin Acids in Fatty Mixtures. D. McNicoll.** (*J. Soc. Chem. Ind.*, 1921, **40**, 124T.)—The author describes a method for the estimation of resin acids in which the inaccuracies of Twitchell's method are avoided, whilst at the same time simplicity is gained by substitution of methyl for ethyl alcohol and of naphthalene-β-sulphonic acid for hydrogen chloride. In a volumetric estimation, 2 grms. of the mixture are dissolved in 20 c.c. of a 4 per cent. solution of naphthalene-β-sulphonic acid in methyl alcohol and heated for thirty minutes under a reflux condenser on an electric plate or oil-bath, a blank experiment with the sulphonic acid solution being carried out simultaneously. The contents of the flasks are then cooled and titrated with $\frac{N}{2}$ solution of potassium hydroxide in methyl alcohol. The resin acids are calculated on the combining weight of 346. For a gravimetric estimation, the neutralised solution of known volume obtained above is transferred to a separating funnel and extracted with an equal volume of ether and petroleum spirit; the soap solution is similarly extracted, the combined extracts are washed with 50 per cent. aqueous alcohol, and the washings added to the resin soap solution, which is acidified and extracted with ether. Pure fatty acids are completely esterified by this process; when it is applied to resin, partial esterification, to the extent of 1 to 3 per cent. of the resin acids, takes place. With three mixtures containing 11·51, 29·84, and 48·69 per cent. of resin, respectively, the results obtained by the volumetric method were 11·84, 30·28, and 48·45 per cent.; and by the gravimetric estimation, 11·73, 30·23, and 48·88 per cent. In a series of tests the errors varied between −0·22 and −0·56 per cent. in the volumetric method, and between −0·38 and +0·35 per cent. in the gravimetric method. Lewkowitsch has shown that by Twitchell's method the errors vary between −9·73 and +5·26 per cent.

W. J. W.

**Apparatus for Estimating the Yield of Tar from Coal. H. Schrader.** (*Brennstoff. Chem.*, 1921, **2**, 182-183.)—A modification of the apparatus for the estimation of tar in coal (*Brennstoff. Chem.*, 1921, **1**, 87; *J. Soc. Chem. Ind.*, 1920, 566A) is described by which steam used in the process is superheated in the apparatus itself. With this object, the supporting arm walls and base of the apparatus are drilled, so that steam introduced through the arm passes vertically downwards, traverses the base in a V-shaped course, and then passes upwards and through the cover into the interior of the retort. Suitable apertures in the retort walls to facilitate cleaning of the steam channels, and means for removing condensed water, are provided. In order to prevent condensation in the retort, steam is not introduced till the temperature has reached 130° C., and the rate of the current is controlled so as to avoid mechanical loss of coal. A small condenser is inserted between the delivery tube and the receiver; the heavy oils which collect in the condenser are separated by treatment with ether, whilst lighter oils are similarly recovered from the final receiver. W. J. W.

**The Setting and Melting Points of Gelatins. S. E. Sheppard and S. Sweet.** (*J. Ind. Eng. Chem.*, 1921, **13**, 423-426.)—In the apparatus described an intermittent stream of air bubbles under constant pressure is passed through the test solution, the latter being cooled with ice-water. A thermometer is immersed in the solution with its bulb adjacent to the air passage, and the temperature at which the bubbles cease to pass is taken as the setting-point. Inversely, after sufficient under-cooling, the set jelly is heated gradually, and the melting-point taken as the temperature at which bubbles again pass through the solution. The compressed air employed passes a manometer and a manostat bottle, and enters a U-tube containing mercury, which serves as a valve to produce intermittence in the air supply; a solenoid, the current through which is made and broken by a timing device every fifteen seconds, effects this interruption by operating an iron plunger. From the U-tube the air passes to a compensating U-tube, and from this to the setting-point tube. The gelatin solutions (1, 3, 5, 10, 15, and 20 per cent. air-dry substance) used are prepared under standard conditions. Results recorded show that the relation between melting-point and concentration is only approximate, and that a similar restriction is true as regards the relationship to jelly strength. W. P. S.

## INORGANIC ANALYSIS.

**Poirrier Blue as an Indicator. W. Mestrezat.** (*J. Pharm. Chim.*, 1921, **23**, 489-494.)—Experiments with a number of samples of this indicator show that the colour changes occurring in the titration of alkali or of mixtures of alkali and alkaline carbonate are progressive, and so much affected by dilution that this indicator compares unfavourably with methyl orange or phenolphthalein. R. G. P.

**Modified Iodine Solution for the Reich Test. H. M. Lowe.** (*J. Soc. Chem. Ind.*, 1921, **40**, 123-124T.)—In the standard iodine solution used for estimating sulphur dioxide in gases the potassium iodide may be replaced by a proportion of sodium hydroxide insufficient to react with the whole of the iodine, but sufficient to form enough sodium iodide to dissolve the remaining iodine. From a solution consisting of iodine, 127 grms.; sodium hydroxide, 30 grms.; and water, up to 10 litres, the theoretical amount of iodine is always found to be liberated on acidification. With a $\frac{N}{10}$ solution no further addition of acid is necessary; but when dilutions of $\frac{N}{100}$ to $\frac{N}{2000}$ are employed, as in testing exit gases, a small amount of sulphuric acid or hydrochloric acid must be added to cause the iodide and iodate in the solution to react instantaneously. W. J. W.

**Detection and Estimation of Traces of Hydrogen Peroxide. F. W. Horst.** (*Chem. Zeit.*, 1921, **45**, 572.)—Traces of hydrogen peroxide may be estimated by reduction with ferrous sulphate solution, and subsequent colorimetric estimation of the ferric sulphate by means of ammonium thiocyanate. In order to obtain the ferrous sulphate solution free from ferric salts, it is placed in a closed Erlenmeyer flask and a current of hydrogen sulphide is passed through it, first in the cold and then during boiling; the solution is then cooled in a current of carbon dioxide.

Twenty c.c. of the sample are placed in a tube, and a few c.c. of petroleum spirit added to form a protective layer against oxidation during the reaction. After addition of 2 c.c. of the ferrous sulphate solution, the mixture is agitated by means of a stream of carbon dioxide freed from oxygen by passing it through ferrous sulphate solution, and 5 c c. of concentrated ammonium thiocyanate are introduced. After further agitation, the colour is compared with that of a standard solution. W. J. W.

**Estimation of Silver by Precipitation with Hypophosphorous Acid. L. Moser and T. Kittl.** (*Zeitsch. anal. Chem.*, 1921, **60**, 145-161.)—Soluble silver salts are readily reduced to colloidal silver by hypophosphorous acid, and this reaction may be employed for their quantitative estimation. At 20° C. the solubility of the silver gel in water was found to be $4 \times 10^{-5}$ g.-ions per litre; in *m*/40 and *m*/400 solutions of hypophosphorous acid the solubility is highest at 50° C., the figures being $4{\cdot}2 \times 10^{-5}$ and $1{\cdot}1 \times 10^{-4}$ g.-ions per litre respectively. Analysis of the reaction product after reduction gave, in four experiments, 7·1 to 8·5 per cent. $H_3PO_4$, 39·6 to 43·8 per cent. $H_3PO_3$, and 48·6 to 51·9 per cent. $H_3PO_2$. The silver colloid contained traces of adsorbed phosphoric acid. The method gives good results when applied to the separation of silver from lead, zinc, or cadmium. W. J. W.

**Separation of Silicon, Tin, Titanium, and Zirconium by Means of Sodium Carbonate. P. Wenger and J. Morel.** (*Ann. Chim. Anal.*, 1921, **3**, 139-142.)—A mixture of the four oxides is ignited, weighed, and then fused with six times its weight of sodium carbonate, the mixture being first heated just to fusion for ninety minutes, and then for the same period over a blowpipe flame. When cold, the fused mass is boiled with water, the solution filtered, and the insoluble portion washed; the filtrate, which contains the silica and a portion of the tin, is evaporated with nitric acid, the residue of silica and metastannic acid collected, ignited, and weighed, and the silica then separated by means of hydrofluoric acid. The insoluble portion from the sodium carbonate fusion contains the remainder of the tin, and the zirconium and titanium oxides; it is ignited, weighed, fused with eighteen times its weight of potassium bisulphate, and the fused mass boiled with water acidified with nitric acid. Metastannic acid remains insoluble, and is collected on a filter, ignited, and weighed; the filtrate is neutralised, the zirconia precipitated by the addition of hydrogen peroxide, collected, and weighed. Titanium is then precipitated from the solution by ammonia. W. P. S.

**Reductions with Zinc and Cadmium in Volumetric Work. W. D. Treadwell.** (*Helv. Chim. Acta*, 1921, **4**, 551-565.)—The use of Jones's reductor for the reduction of ferric salts was investigated; it was found that reduction was complete with a 2·5 cm. column of granulated zinc if the ferric solution was admitted drop by drop. Using a 9·5 cm. column, complete reduction was attained, even on rapid percolation. A moderate degree of acidity favours the rate of reduction, whilst precipitation of metallic iron need not be feared in solutions containing 2 per cent. of sulphuric acid. The risk of precipitating metallic iron is quite obviated by the use of cadmium as a

reducing agent. A 5 cm. column of crystalline electrolytic cadmium free from sponge gave rapid and complete reduction with various degrees of acidity, and a small cadmium consumption. A preliminary investigation was made regarding the efficiency of the cadmium reductor in the volumetric estimation of titanium, molybdenum, vanadium, and uranium; very promising results have so far been obtained. W. R. S.

**Estimation of Total Carbon and New Method for Graphitic Carbon in Ferro-Alloys. P. Wenger and A. Trampler.** (*Helv. Chim. Acta.*, 1921, **4**, 547-551.)—The total carbon was determined in various ferro-alloys by combustion in an electric furnace at 1,150° C., and by Corleis' method (chromic-sulphuric acid mixture). It was found that the results obtained by combustion were higher and more concordant; combustion is also quicker, and applicable to any ferro-alloy; hence it is the best practical method. In the combustion of ferro-alloys of chromium, molybdenum, silicon, and manganese, the use of an oxidiser is necessary; bismuth sesquioxide is recommended. Sulphur dioxide is retained in a heated porcelain tube containing lead chromate. Graphitic carbon may be estimated in ferro-manganese, -vanadium, -chromium, and -silicon by digesting 1 grm. of the powdered alloy with 100 c.c. of phosphoric acid of sp. gr. 1·7; the acid is first heated to 150° C. in a platinum dish; the powder is then gradually added. The heat is raised to 230° to 250°, the acid is decanted, and the attack completed with 25 c.c. of fresh acid. The undiluted liquid is filtered on a Gooch crucible, and the residue is washed with 300 c.c. of water, dried, and treated by combustion in an electric furnace. In the case of ferro-silicon, hydrofluoric acid must be added to the phosphoric acid, but even this mixture fails if the silicon exceed 60 to 65 per cent. W. R. S.

**Volumetric Estimation of Aluminium in its Salts. A. Tingle.** (*J. Ind. Eng. Chem.*, 1921, **13**, 420-422.)—Investigation of various procedures which have been suggested for the titration of aluminium salts with alkali solution, using phenolphthalein as indicator, showed that two only are reliable. The first consists in titrating the boiling solution containing the aluminium salt with $\frac{N}{2}$ sodium hydroxide solution until the pink coloration obtained with the phenolphthalein added persists after boiling for one minute. In the second method, which is particularly applicable to aluminium sulphate, 100 c.c. of a 1 per cent. solution of the salt are boiled, treated with 5 c.c. of saturated barium chloride solution, and then titrated while hot, as described. The advantage attained by the addition of the barium chloride is that basic aluminium chloride is less stable and more soluble than the basic sulphate, and, further, the precipitated barium sulphate completely masks the colour of iron salts if these be present. It is important that the concentration of the alkali solution used should not be greater than $\frac{N}{2}$. If the titration be carried out on the cold solution, basic salts form and interfere, and the end-point is obscured because the precipitate does not settle readily. There is no advantage in the use of barium hydroxide solution in place of sodium hydroxide solution. W. P. S.

**Production and Testing of Zirconia. W. R. Schoeller.** (*J. Soc. Chem. Ind.*, 1921, **40**, 127-128T.)—The method of extracting zirconia from Brazilian ores, based on precipitation of zirconium as basic sulphate (Rossiter and Sanders, *J. Soc. Chem. Ind.*, 1921, 70T), does not eliminate titanium, which is present to the extent of 0·6 to 1·2 per cent. It may be completely removed by recovering the zirconium as oxychloride, but this operation is more expensive. A combined oxychloride and basic sulphate method is considered by the author to repay further investigation. The ore is fused with sodium carbonate and extracted with hot water, the recovered alkali being used for treating further ore. The insoluble residue is treated with the zirconium oxychloride wash-liquors, the solution evaporated to dryness, and the mass extracted with hot water. After filtration, the filtrate is mixed with hydrochloric acid and crystallised; the crystals are filtered off, washed with hydrochloric acid, heated to expel water, and finally boiled with dilute ammonia and ignited. The acid used for washing the oxychloride, mixed with some of the oxychloride mother-liquor, is used again to dissolve the fused residue, whilst the remainder of the mother-liquor is neutralised and treated with sulphurous and sulphuric acids. The zirconia obtained is free from iron and alumina; for removing titania, fractional solution or precipitation may prove suitable. Commercial zirconia may contain, in addition to iron, aluminium, and titanium, appreciable amounts of silica, arsenic, and sulphite; in some samples, lime, sodium carbonate, fluorine, chlorine, carbon dioxide, and boron trioxide, have been found. For the estimation of arsenic, 2 grms. are fused with 15 to 20 grms. of sodium carbonate, extracted with hot water, acidified, and treated with hydrogen sulphide, preferably after addition of potassium iodide to reduce arsenious acid. The sulphide is then evaporated with sulphuric acid till fumes are evolved, and the liquid is made alkaline with bicarbonate and titrated with iodine solution. W. J. W.

**Gasometric Estimation of Hypochlorites. A. K. Macbeth.** (*Chem. News*, 1921, **122**, 268.)—Hypochlorites may be accurately estimated by treating them in a Van Slyke nitrometer (*J. Biol. Chem.*, 1912, **12**, 278), with an alkaline solution of hydrazine (prepared by dissolving hydrazine sulphate and potassium hydroxide in water), and measuring the nitrogen evolved. Free chlorine must be absent. In one set of experiments this method gave 16·13 grms. potassium hypochlorite per litre, as compared with 16·063 and 16·11 grms. by titration with arsenious acid and sodium thiosulphate respectively; further comparative results by the three methods were 23·55, 23·54, and 23·55. The method may be used for estimating available chlorine in bleaching powder. It has not given satisfactory results when applied to the estimation of chlorates. W. J. W.

**Examination of Detonators and Percussion Caps. A. Langhans.** *Zeitsch. ges. Schiess.- u. Sprengstoffw.*, 1921, **16**, 49-52, 57-59.)—Detonator and percussion-cap compositions containing as ingredients mercury fulminate, potassium chlorate, antimony sulphide, powdered glass, gunpowder, and shellac, may be identified by a microscopic examination, as well as, to some extent, by their behaviour with concentrated acids. For the quantitative examination a method is described in which both

the composition and its container are brought into solution and then submitted to analysis; by this means any risk involved in removing the composition from the shell for testing is eliminated. About four percussion caps are dissolved in a mixture of 50 c.c. of nitric acid and 25 c.c. of water. The solution is evaporated to dryness, and the residue, after boiling three times with dilute nitric acid, is filtered, by which means powdered glass, together with some charcoal and sulphur, is separated. After dilution of the filtrate to 500 c.c., 100 c.c. are treated with hydrogen sulphide, and the sulphides of mercury and antimony in the precipitate are dissolved by treatment with sodium sulphide solution and potassium hydroxide; the residual copper sulphide is removed by filtration, dissolved in acid, and electrolysed. The filtrate is acidified, and the antimony sulphide separated by treatment with ammonium sulphide and precipitation with sulphuric acid; the mercury sulphide is dissolved in nitric acid and electrolysed. Chlorate and nitrate of potassium are estimated in the original filtrate from the hydrogen sulphide precipitation. With detonators containing a mixture of potassium chlorate and fulminate of mercury, a similar method may be applied; estimation of the chlorate by the use of nitron is also suitable.

W. J. W.

## PHYSICAL METHODS, APPARATUS, ETC.

**Apparatus for Microscopic Examination of Opaque Objects. M. Francois and C. Lormand.** (*Bull. Soc. Chim.*, 1921, **29**, 366-374.)—Opaque objects are illuminated by rays of light focussed on the object from a small concave mirror of polished silver or white metal (about 1 mm. in thickness) fixed to the end of the objective, and pierced by a central hole (about 1 mm. in diameter) through which the object is viewed; each objective requires a mirror of such curvature that the light is accurately focussed on the object when the latter is in focus on the microscope stage. An electric lamp (2 to 3 volts) with a bulb of lenticular shape (about 2 cm. in diameter), having a metallic filament of lozenge or **S**-form, and mounted in a tube with a lens to render the rays parallel (an eyepiece without the lower lens), is fixed below the stage, so as to throw parallel rays of light on to the mirror. The light is prevented from passing directly from this source to the objective by mounting the object on a dark-ground of such dimension as to obscure the field visible with any particular objective. The dark-grounds are conveniently made by cutting thin discs from rods (0·75 to 3·0 mm. in diameter) composed of a mixture of kaolin and ground quartz; the discs are then fired at red heat, and (after colouring any shade required) are mounted on a slide with Canada balsam. Examination of objects by this apparatus is best conducted in a dark room. A small electric lamp, as described above, as a source of illumination is suitable for transparent objects, and it is suggested that it may conveniently replace the ordinary reflecting mirror, as the illumination is constant and easily regulated by interposing screens of paper between the source of illumination and the slide.

R. G. P.

**Use of Polarised Light for the Examination of Old Pictures. P. Lambert.** (*Comptes rend.*, 1921, **172**, 1476-1477.)—Even under the best conditions, the image diffused by the colours of old pictures is always attenuated and whitened by the

light reflected from the surface. If, however, the picture be illuminated by means of polarised light, and examined through a Nicol prism, the reflected light will be extinguished if the prism be in the position of extinction; whereas that which traverses the varnish is depolarised at the surface of the materials composing the colours, and is thus able to reach the eye. The method gives results of value in the judging of old pictures, and in indicating a possible improvement by modification of the varnish. T. H. P.

**New Method of Measuring Electrolytic Conductance. C. Marie and W. A. Noyes, jun.** (*J. Amer. Chem. Soc.*, 1921, **43**, 1095-1098.)—The hydrogen electrodes used consisted of vertical glass tubes connected at the lower end with a small glass box, one side of which was made of fine platinum gauze and connected with the Wheatstone bridge by a platinum wire. A current of purified hydrogen, which was bubbled through a solution having the same composition as that under examination, was passed down the tube, and escaped through a small aperture in the bottom of the box. The electrodes were immersed in the solution, adjusted to equal potential by carefully regulating the gas pressure in each, and a direct current passed for only a sufficient length of time to indicate the direction of deflection of the galvanometer. A series of determinations, using different inorganic and organic acids and sodium chloride solutions of various strengths, gave results in exact agreement with those obtained by the authors using Kohlrausch's alternate current method, except with sulphuric and hydrochloric acid solutions of greater concentration than $\frac{N}{2}$. T. J. W.

**Rapid Method for Measuring the Auto-discharge of an Electroscope in the Estimation of Radium Emanation. P. Loisel.** (*Comptes rend.*, 1921, **172**, 1484-1486.)—In the ordinary method for measuring radium emanation, the discharge current, $I_d$, of the electroscope is first observed, the emanation being then introduced, and the true intensity of the maximum current, $I_m$, measured three hours later, calculated by subtracting the former from the latter current. Since the auto-discharge current of the electroscope is subject to considerable variation, particularly in the neighbourhood of radioactive sources, this method may lead to erroneous results. Sensible error may be avoided as follows: The intensity, $I_1$, of the ionisation current produced in the condenser is measured three hours after the introduction of the emanation: $I_m = I_1 - I_d$. The condenser is then rapidly exhausted and filled with inactive air; the emanation being removed, only the induced activity remains, and the current produced is $0{\cdot}57\ I_m$. If the ionisation current fifteen minutes after the evacuation be $I_2$, $0{\cdot}285\ I_m = I_2 - I_d$, so that $I_d = \frac{I_2 - 0{\cdot}285\ I_1}{1 - 0{\cdot}285}$. T. H. P.

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## NEW BRITISH CHEMICAL STANDARD STEELS.

(Analytically Standardised Turnings.)

Two new plain carbon steel standards are now ready for issue—viz., "M," needed for some time mainly for colour carbon tests round about 0·23 per cent.; and "01," which fills the vacancy for a colour carbon standard of about 0·33 per cent., in addition to being available for the other elements shown below.

The analyses have been undertaken, as usual, by a number of experienced chemists representing the following interests: British Government Department; U.S. Bureau of Standards; Referee Analysts, independent; Railway Analysts, representing users issuing specifications; and Works Analysts, representing makers and users.

The standard figures ("M" and "01") are as follows:

Carbon, 0·228 and 0·335; silicon, 0·057 and 0·162; sulphur, 0·04* and 0·032; phosphorus, 0·04* and 0·031; manganese, 0·58* and 0·617; arsenic, 0·024; chromium, 0·017; copper, 0·037; nickel, 0·162.

The standards may be obtained either direct from Organising Headquarters, 3, Wilson Street, Middlesbrough, or through any of the laboratory furnishers, at a price just sufficient to cover the cost. A certificate giving the names of the analysts co-operating, the types of methods used, and a detailed list of their figures will be supplied with each bottle.

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## REVIEWS.

Physical and Chemical Constants. By G. W. C. Kaye, O.B.E., D.Sc., and T. H. Laby, M.A. Pp. 161. London: Longmans, Green and Co. 1921. Price 14s. net.

The fact that this is the fourth edition since the appearance of the first edition in 1911 is sufficient proof alone of the value of this book. The new edition follows closely the lines of earlier editions, but various alterations and additions have been made in the sections dealing with such questions as the figure of the earth and the absolute determination of the acceleration of gravity, whilst the chemical data have been recalculated on the basis of the 1920-21 atomic weights. The tables of physical constants of chemical compounds have been altered and enlarged.

This book contains a very large amount of data to which the research chemist, and particularly the physical chemist, needs to refer, and the covering of a very wide field in a conveniently condensed form renders it most useful for reference purposes, whilst the very copious references to standard works and original papers enhances its value. R. G. Pelly.

Tables of Refractive Indices. Vol. II. Oils, Fats, and Waxes. Compiled by R. Kanthack, edited by J. N. Goldsmith, Ph.D., M.Sc., F.I.C. Pp. 295. London: Adam Hilger, Ltd. 1920. Price 25s. net.

Vol. I. of this work, which dealt with essential oils, has been reviewed in this journal (1919, **44**, 306), and Vol. II, which is now before us, is compiled on similar lines.

* Approximate.

The compilation includes the results of some 1,750 measurements on over 500 oils, fats, and waxes, and gives approximately 2,500 references to the original literature. The compiler in his wisdom has clearly pointed out in the Preface that it is not within his province to accept or reject data, and thereby he shows that he is well aware that quite a number of published figures of refractive indices are not worth the printer's ink. These worthless figures, like the tares and wheat, have been allowed to grow side by side with reliable ones in scientific literature, and the compiler has gathered them together in this work, leaving the reader to cast out the tares, the weeding out of which is now rendered less difficult by comparison with the many reliable figures so conveniently tabulated.

The collection of data distributed over such a wide expanse of literature cannot fail to impress one as to the patience which such a task involved, and such a collection in a form so convenient for reference will appeal to the practical analyst.

E. R. BOLTON.

THE CHEMISTRY OF SYNTHETIC DRUGS. By PERCY MAY. Third Edition. Pp. xii + 248. London: Longmans, Green and Co. 1921. Price 12s. 6d. net.

In the first forty-three pages of this book Dr. May gives an admirable outline of the relation between chemical constitution and physiological action; in easy style the present knowledge is summarised, and if the conclusions are somewhat incomplete, it is due to the fact that only the fringe of the subject has yielded to investigation.

The remainder of the work is devoted to the chemistry of synthetic drugs, and the author is singularly happy in the manner in which he has classified them; it is practically impossible to find any classification in which no overlapping occurs, but that adopted affords the minimum of such overlapping. The plan adopted is to give the chemical constitution of each substance, with a brief but sufficient indication of its action, with useful comparisons of the difference in action of allied substances.

Little or no attempts are made to give the mode of preparation of the drugs, and the analytical characters are omitted, the author sticking entirely to the chemistry of the subject with a complete absence of padding. A careful search has failed to reveal the absence of any synthetic drug of any importance, and, indeed, the only noticeable omissions are those of alternative names such as glusidum, the B.P. name for saccharin, and uradal, given in the B.P.C. for adalin.

There is no doubt that public analysts and those engaged in the examination of drugs who wish to keep their knowledge of the chemistry of the substances they examine up to date will find this book invaluable. H. DROOP RICHMOND.

THE CHEMISTRY AND ANALYSIS OF DRUGS AND MEDICINES. By HENRY C. FULLER. Pp. 1072. New York: John Wiley and Sons. 1920. Price 55s. net.

Published works on the analysis of drugs and medicines are comparatively few. The analyst engaged in purely pharmaceutical analysis has to draw his textbook information from a wide range of works, none of which deal with drugs as the chief subject. Apart from sections of Allen's "Commercial Organic Analysis" and certain

chemico-pharmaceutical works, such as Squire's "Companion," we have in this country to rely on works in which drugs take second place to foods. It was, therefore, with a hope that this gap would in some measure be filled that the reviewer turned to the present work.

The book under review is divided into five parts as follows:

I. General Methods and Crude Drug Assays.
II. Alkaloidal Drugs, Alkaloids, and Medicinally Allied Substances.
III. Glucosides, Glucosidal Drugs, and Natural Drugs containing Principles other than Alkaloids.
IV. Organic Substances other than Alkaloids and Glucosides.
V. Inorganic Section.

It may be said at once that this work is mainly devoted to the analysis of naturally occurring and synthetic organic drugs. The inorganic section of the work occupies only a small space by comparison. Whilst acknowledging that the classification of drugs for a book of this kind is a difficult matter, it must be said that the arrangement of the book is certainly open to criticism; in fact, the more one seeks to discover the basis of the arrangement, the more illogical does the latter appear. In dealing with this point, it is well to inquire from what standpoint the author has written. The predominant idea of the book seems to be the analysis of unknown remedies and the determination of their constituents, whilst the determination of the purity of drugs is a secondary consideration. For this reason the introductory chapter on General Methods deals with the following at first sight somewhat curiously chosen determinations—viz.: Specific Gravity, Ash, Alcohol, Cane Sugar, Glucose Syrup, and Arsenic. There follows a chapter on Crude Drug Assays, chemical and physiological; the greater portion consists of a reprint of the U.S. Pharmacopœia methods, and in many cases both the methods of the eighth and ninth revisions are given, but without any expression of opinion as to which is the better of the two. It is not easy to see why the drugs here included are thus separated from their fellows. The determination of morphine in opium and tincture of opium is to be found in this chapter, but powdered opium, paregoric, and laudanum are found in Chapter VII. Natural drugs are divided into the following: (1) Alkaloidal Drugs, (2) Glucosidal Drugs, (3) Purgative Drugs, (4) Miscellaneous Acting Drugs, and (5) Botanical Drugs. The title of the fourth division might have been more happily expressed, but the meaning of the fifth is distinctly puzzling. It might be meant to include those drugs that do not "act," but on inspection it is found to include *Cannabis Indica*, *Leptandra*, and many others not by any means innocuous. The inclusion of anæsthetics such as chloretone in the chapter on alkaloids derived from pyrrolidin, of columbin under alkaloids derived from isoquinoline, of kino among gums and resins, seems hardly justifiable.

The best feature of the book, and the most valuable to analysts generally, is the inclusion of descriptions of a large number of synthetic and proprietary remedies; many of them, it is true, are unknown or little used in this country, but much useful information is scattered throughout the book. The notes on the uses of the various drugs and the combinations in which they are most likely to be found should also be of great value to the analyst.

The sections dealing with alkaloids and glucosides are on the whole full and well written.

Essential oils and fixed oils are lightly treated, occupying together only twenty-four pages, so that naturally there are many omissions. Cod-liver oil is fully treated, but the limits of specific gravity seem very narrow—viz., 0·9196 to 0·922 at 25° C. In discussing the therapeutic value, no reference is made to what is now known to be the chief factor in the peculiar virtue of cod-liver oil, its high content of fat-soluble vitamin.

The analytical methods are chiefly drawn from American sources; many of them are probably unfamiliar, by name at any rate, to English readers. From an examination of the familiar methods included, it does not appear that any great discrimination has been used in their selection—*e.g.*, the discredited lead number test for asafœtida is given in spite of the work of Harrison and Self (*Pharm. J.*, 1913, 218). On p. 653 it is stated that "there is no method for determining the relative quantities of citric and tartaric acids in a mixture of the two"; on p. 650 we find, "when tartaric acid occurs simultaneously with citric acid, the potassium method will give good results"; and on p. 655 is given the useful mercury method of Gowing Scopes (ANALYST, 1913, **38**, 12) for the same purpose.

On p. 491, evidently by a misprint, −70 is given as the minimum rotation of copaiba oil.

On p. 750 the solubility of calcium glycerophosphate is erroneously given as 1 : 400.

To sum up, it may be said that the book will provide much useful information to the analyst who has to deal with unknown mixtures of drugs or medicines. Its value to the analyst in a pharmaceutical works, or to one who is primarily engaged in assaying or testing the purity of drugs, is considerably less; for though he may turn to it occasionally for information, he is hardly likely to use it as a standard textbook of drug analysis. NORMAN EVERS.

ANIMAL AND VEGETABLE FIXED OILS, FATS, BUTTERS, AND WAXES. By C. R. ALDER WRIGHT. Third Edition, revised and greatly enlarged by C. AINSWORTH MITCHELL. Pp. 939. London: Charles Griffin and Co., Ltd. 1921. Price 56s. net.

The second edition of this work, published in 1903, has been out of print for the last two years, but earlier revision has been prevented by the war. As the reviser states, the literature of the subject has multiplied very greatly during the past few years, and it has become necessary to make a selection from the mass of material available. Even so, the volume has increased from 804 to 939 pages, partly due to the fact that the section on margarine has been rewritten, and a new chapter on hydrogenated oils added; while the International Standard methods for glycerine analysis are incorporated in the last chapter, and an official report from the Ministry of Food on Standard Methods of Analysis of Seeds, Nuts and Kernels, Fats and Oils, and Fatty Residues, and a summary of recent work on vitamins in relation to fats, are included as appendices.

In the preparation of the second edition the aim was to fit it particularly for use as an analytical textbook, and this characteristic of the work is still maintained, both as regards raw materials and the manufactured products, the recorded values for the individual oils being brought up to date, and the more recently introduced analytical processes described. It is a pity that, although such useful methods as those of Polenske and Kirschner are given fairly fully, just sufficient data are omitted to render it impossible for the novice to carry out the determinations without seeking information elsewhere, and it is surely time that the phrase "a few fragments of pumice" should disappear from the Polenske process, and give place to the correct "0·1 grm. of powdered pumice." Probably few analysts would consider ten minutes' contact long enough for determining the iodine value of linseed oil by the Wijs method, two hours, as prescribed by the British Pharmacopœia, being much more satisfactory. Under Chinese wood oil, Hoepner and Burmeister are quoted as getting untrustworthy results by the methods of Wijs and Hanus, but by adopting Chapman's method (ANALYST, 1912, p. 545), dissolving 0·1 grm. of oil in 20 c.c. carbon tetrachloride, adding 30 c.c. Wijs' solution, and allowing to stand for three hours before titration, perfectly satisfactory results may be obtained. No reference is made to the Ave-Lallemant method of examining butter-fat (ANALYST, 1907, p. 382), and it is surprising in a book of this character to find the only method given for estimation of boric acid is that of distillation with methyl alcohol.

The description of the individual oils and fats covers all the more important varieties, but it is disappointing to find only carnauba wax under the "vegetable non-glyceridic waxes," no mention being made of candelilla, esparto or reed, and sugar wax, although these are all of technical importance. The expression "non-glyceridic wax" itself appears open to objection, as all true waxes are necessarily non-glyceridic, and it is rather regrettable that this distinction between fats and waxes is not made more clear both in the introductory chapter and in the classification on p. 370.

The statement on p. 692 that bees fed on sugar are incapable of developing wax to any notable extent is incorrect, several experimenters having shown that bees fed on sugar produce more wax than those fed on honey.

The chapter on hydrogenation of oils outlines the more important patents for plant, preparation of catalyst, and hydrogenation process. The properties of hardened oils are described, and the dimethyl-glyoxime test is given as the best for the detection of nickel, but no mention is made of the extremely sensitive $\alpha$-benzil-dioxime method for the detection and estimation of this metal. The sections on technology remain much as before, descriptions of the Twitchell and castor ferment methods for fat-splitting being now included, and also modern plant for the concentration and distillation of glycerin. The rewritten section on margarine gives a useful and up-to-date review of the modern developments in this industry.

The book is well printed and illustrated, though one or two of the blocks in the soap section are a little out of date. Owing to an obvious error in setting up on p. 502, the description of rape oil appears under radish-seed oil, but there are very few misprints, only two or three trivial ones being detected. The reviser is to be congratulated on the vast amount of information he has brought together within the confines of a single book.

W. H. SIMMONS.

REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY. Vol. V. 1920. Issued by the Society of Chemical Industry. Price 8s. 3d. to members, 15s. to non-members, post free.

In these days, when the high prices of books, particularly of those on technical and scientific subjects, show no sign of a downward tendency, the Society of Chemical Industry is to be congratulated on its ability to issue the "Annual Reports" at the very moderate charge demanded, the volume representing excellent value for the money, even at the price asked of non-members of the Society. That the "Reports" should be in the hands of every chemist is beyond question, and if a poll of the members of the Society were taken, objectors to the inclusion of the price in the annual subscription would assuredly form only a small minority.

Vol. V. follows, in the main, the paths laid down by its predecessors, the twenty-seven sections into which it is divided corresponding approximately with the headings under which the abstracts published in the Society's journal are grouped.

In view of the high cost of fuel now prevailing, and of the consequent necessity for economy in its consumption, the widest appeal to those engaged in industry is made by the first few sections, in which such matters as fuel in general, boiler plant, steam production, liquid and motor fuels, power alcohol (referred to also in several of the later sections), and the like, are considered. The section of greatest interest to the members of our own Society is that under the title "Analytical Chemistry," now for the second time from the experienced hands of Mr. C. A. Mitchell. This section deals principally with such analytical methods as are more especially of technical interest, and may usefully be read in conjunction with the chapter—also due to Mr. Mitchell—under the same title in the "Annual Report of the Progress of Chemistry for 1920," issued by the Chemical Society. Analytical processes are given a place also in certain of the other sections.

In general, the contributors have done their work thoroughly and with discrimination, and although it may be felt that some of the matter dealt with deserves more than the passing notice actually bestowed on it, the rigid rationing of space necessary with a composite compilation of this character must be held responsible.

As in former years, the book is printed in a good, readable type, and few errors, typographical or otherwise, are evident. Its value is greatly enhanced by the excellent author and subject indexes. T. H. POPE.