MAY, 1933 Vol. LVIII., No. 686

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 5th, the President, Mr. F. W. F. Arnaud, being in the chair.

Certificates were read in favour of George Vincent Hall, M.Sc., A.I.C., Geoffrey Holland, B.Sc., A.I.C., Herbert Stanley Howes, B.Sc., F.I.C., Frederick William Moore Jaffé, B.Sc., A.I.C., and Malcolm McFarlane Love, F.I.C.

The following were elected Members of the Society:—Gilbert Fatkin Caley, William Robert Dracass, B.Sc., and Y. V. Srikanteswara Iyer.

The following papers were read and discussed:—"Notes on the Iron and Copper in Liver and Liver Extracts," by H. G. Rees, B.Sc., A.R.C.S., A.I.C.; and "The Determination of the True Freezing-Point of Milk," by G. W. Monier-Williams, O.B.E., M.C., M.A., Ph.D., F.I.C.

NORTH OF ENGLAND SECTION

A MEETING, called by the Section, was held in Manchester on April 8th to consider the question of the application of the freezing-point test to milk as a means of detecting the presence of added water.

The Chairman (Mr. J. Evans) presided over an attendance of sixty-four.

The discussion was introduced by Dr. G. W. Monier-Williams, M.A., F.I.C. who also exhibited his new design of freezing-point apparatus (see p. 254).

After discussion, several resolutions, relating to the subject of the freezing point of milk, were passed for submission to the Council.

A resolution of condolence with the relatives of the late Mr. James Wood was passed.

The Determination of the True Freezing Point of Milk

By G. W. MONIER-WILLIAMS, M.A., Ph.D., F.I.C.

(Read at the Meeting, April 5, **1933**)

THE determination of the freezing point, first applied to the detection of added water in milk by Beckmann and Jordis in 1895, has now become a routine operation in many laboratories. In a report to the Local Government Board in 1914 I reviewed the extensive literature of the subject up to that time, and gave the results obtained from 141 samples of milk from single cows and from herds. The apparatus that I used was too elaborate for routine work. It was extensively modified and standardised by Hortvet (*J. Ind. Eng. Chem.*, **1921**, **13**, 198), and his "cryoscope" was officially adopted by the Association of Official Agricultural Chemists in the United States. The method did not become general in this country until after the publication of papers by Elsdon and Stubbs (ANALYST, **1930**, **55**, 423; *J. Soc. Chem. Ind.*, **1931**, **50**, 135T). These authors gave a full description of the Hortvet cryoscope, and emphasised the value of the freezing-point method in the examination of milk.

THE HORTVET CRYOSCOPE.—The Hortvet cryoscope is a standardised apparatus, and gives results which, while they do not purport to represent accurately the true freezing point of milk, *i.e.* the temperature at which milk is in exact equilibrium with ice, are yet strictly comparable and reproducible with a fair degree of precision. The same thing may be said, more or less, of several other forms of apparatus which have been adopted, officially or semi-officially, in other countries (Holland, Germany, New Zealand, etc.). Suggestions have been made at various times that the figures should be corrected so as to represent more nearly the true freezing point of milk, but these suggestions have not usually been adopted, owing, no doubt, to uncertainty as to the nature and magnitude of the corrections to be applied. It has been considered preferable to adhere, for administrative purposes, to the apparent freezing point, as determined by a standard cryoscope, rather than to confuse matters by attempting to apply corrections which may, or may not, be themselves correct.

This is a perfectly sound attitude, and this paper is intended not as a criticism of the Hortvet cryoscope as used in administrative work, but as an attempt to elucidate the nature and magnitude of the corrections which must be applied if it is desired to ascertain the true freezing point of milk or of any aqueous solution.

THE TRUE FREEZING POINT.—The accurate determination of freezing points has been the subject of investigation by many workers, chiefly on account of its importance in connection with the theory of dilute solutions. A long paper by Raoult (*Z. physikal. Chem.*, **1898**, **27**, 617) contains, perhaps, the best account of the errors to which the measurement is liable and of the corrections which must be applied. In the various forms of cryoscope in common use we do not, as a rule,

find precautions taken to ascertain and apply the supercooling correction, or to isolate the solution at the moment of freezing from the disturbing influence of the surrounding medium. Yet we find that almost all workers, whatever the type of apparatus used, agree that the average freezing point of milk is in the neighbourhood of $-0{\cdot}550°$ C. Moreover, we find that in expert hands these instruments give quite concordant results. The fact is that it is comparatively easy to determine the *approximate* freezing point of a solution. The ice present acts as an almost perfect buffer against the effect of outside influences. Any gain or loss of heat at the freezing point causes a little of the ice to melt or a little more ice to be formed, and the temperature remains approximately constant. Owing to the high latent heat of ice-formation, a comparatively large amount of heat can enter or leave the freezing-vessel without any considerable effect being exerted upon the apparent freezing point of the solution. Thus it is possible to determine the approximate freezing point without taking elaborate precautions to ensure the heat isolation of the liquid.

It is when we come to the determination of the true freezing point, that is to say, the temperature at which the solution itself is in exact equilibrium with ice, that the chief difficulties are met with. The separation of solid ice necessarily implies a corresponding concentration of the solution, and the observed freezing point is the temperature at which the more concentrated, not the original solution, is in equilibrium with ice. It is only by controlling and ascertaining the amount of ice formed that we can obtain the data required to calculate the true freezing point of the original solution.

The amount of ice formed depends upon three things: (i) the extent to which the solution is supercooled before freezing starts; (ii) the water value of the container, the thermometer bulb and the stirrer; (iii) the amount of heat-exchange taking place with the surrounding medium from the time that freezing starts to that at which the final reading of temperature is made.

I propose to consider in detail the effect of each of these three factors, and the corrections necessary for them.

(i) THE SUPERCOOLING CORRECTION.—If we start with x grms. of a dilute aqueous solution, supercool it one degree, and then cause it to freeze, the temperature rises sharply through one degree to the apparent freezing point. The heat required to raise x grms. of water one degree in temperature is x calories. This heat is supplied from the latent heat of formation of ice. Since 80 calories are liberated by the formation of one grm. of ice, the liberation of x calories implies the formation of $x/80$ grms. of ice. The actual quantity of solution, therefore, when equilibrium is established, is $x - x/80$ grms., *i.e.* the solution has been concentrated by approximately 1/80th of its original volume. The true freezing-point depression is, therefore, 1/80th less than the observed depression for every degree of supercooling. We have

$$C = C' - 1/80\, C'S,$$
$$\text{or} \quad C = C' - 0{\cdot}0125\, C'S$$

where C represents the true freezing-point depression, C′ the observed depression, and S the degrees of supercooling. Thus for one degree of supercooling an observed

freezing point of $-0{\cdot}500°$ C. would correspond with a true freezing point of $-0{\cdot}494°$ C., a difference of $0{\cdot}006°$ C.

The value 0·0125 may be termed the theoretical supercooling correction for a very dilute aqueous solution. Most solutions have a slightly smaller specific heat than water, which will tend to make the correction smaller. The specific heat of milk is about 0·93 (Hammer and Johnson, *Agric. Exp. Sta. Iowa State Coll., Research Bull.* 14, 1913), and the value 0·0125 in the above expression would therefore be, for milk, $0{\cdot}0125 \times 0{\cdot}93 = 0{\cdot}0116$.

(ii) THE WATER-VALUE OF THE CONTAINER, THERMOMETER-BULB AND STIRRER.—The thermometer-bulb, the stirrer, and the walls of the containing vessel have all participated in the lowering of temperature involved in the supercooling of the solution, and have to be raised again to the temperature of the apparent freezing point. The heat required for this can be provided only by the formation of more ice, and, consequently, the solution becomes more concentrated, and the apparent freezing point is lowered. In most forms of apparatus the thermometer-bulb and the container are rather large and heavy compared with the amount of liquid present, and their water value is relatively high. The result is that the supercooling correction is considerably increased. The expression

$$C = C' - 0{\cdot}0125\, C'S$$

becomes

$$C = C' - KC'S \qquad \text{(I)}$$

where K has a value of 0·013 to 0·017, or even higher.

It should be noted that the correction to be applied is directly proportional to the amount of supercooling. Thus, if the apparent freezing point of a given solution is determined for different amounts of supercooling, and the results are plotted on squared paper, a line drawn through these points is, over the short range in question, practically straight (*cf.* Fig. 2). From it the true freezing point for supercooling nil can be ascertained, and the supercooling correction K then calculated from Equation I above. Raoult found in this way that the value of K for potassium chloride solution in his apparatus was 0·013, and for sucrose 0·016. With the apparatus described below I have found for sucrose solution in a glass freezing-vessel 0·018, and in a metal vessel 0·017. For milk in glass and in metal the values were 0·017 and 0·014, respectively. I do not think, however, that it is possible, without taking special precautions which are unsuited to a routine method, to determine the value of K with a degree of accuracy much greater than ±0·002. This will involve an uncertainty of ±0·001 in calculating the true from the apparent freezing point of milk. With Hortvet's apparatus, for reasons discussed later, it is a difficult matter to determine K satisfactorily.

(iii) THE HEAT-EXCHANGE WITH THE SURROUNDING MEDIUM.—In order that the temperature in the inner vessel of the Hortvet apparatus may fall sufficiently rapidly, alcohol is introduced into the space between the inner and outer vessel to act as a heat-conducting medium. If this is not done, the rate of cooling is so slow that the method is unsuitable for routine work. Clearly this action of the alcohol continues at much the same rate during the time that the temperature is rising from the lowest point reached to the freezing point. During this time heat is continually being abstracted from the solution, and this loss of heat implies

the formation of more ice in the solution, which thereby becomes more concentrated. The actual amount of ice thus produced will depend upon several things; the temperature of the cooling medium, the thickness and material of the inner and outer freezing vessels and the width of the space between them, the amount of alcohol or other heat-conducting liquid introduced into this space, etc. In Pritzker's apparatus, widely used in Germany, no jacket of any kind is used, and the freezing vessel is immersed directly in the freezing mixture. It would seem that this arrangement must increase appreciably the amount of heat-transference. Raoult used an air-jacket throughout, and, by carefully adjusting the temperature of his cooling medium, avoided altogether the error due to heat transference. He pre-cooled his solutions to 0° C. in a separate ice-bath, and did not attempt to get rapid cooling in his freezing-point apparatus. In the apparatus described by me in **1914** (*loc. cit.*) means were provided for removing the conducting liquid from the jacket and replacing it by air before the actual freezing was started. In this way the solution, at the moment of freezing, was isolated as far as possible from the disturbing influence of the cooling medium.

If we assume for the moment that the heat transference factor is the only one to be considered, we may write

$$C = C' - K'C' \quad .. \quad .. \quad .. \quad .. \quad (II)$$

where C and C′ are, respectively, the true and observed freezing-point depressions, and K′ is a factor depending on the amount of heat transference taking place during the time that the temperature is rising from the lowest point reached to the freezing point. By combining the expressions I and II we arrive at

$$C = C' - C'\,(KS + K') \quad .. \quad .. \quad .. \quad (III)$$

This is the expression connecting the observed with the true freezing-point depression in any form of apparatus. KS + K′ may appropriately be called the "ice correction," since it is a measure of the amount of ice in the liquid. In the Hortvet cryoscope, where the amount of supercooling, S, is always about one degree, the expression becomes

$$C = C' - C'\,(K + K') \quad .. \quad .. \quad .. \quad (IV)$$

Since the amount of heat transference is not directly proportional to the amount of supercooling, the value of K′ cannot be determined by the method shown in Fig. 2. It can, however, be approximately ascertained in the following ways:

(*a*) *Measurement of the rate of temperature-change during a freezing-point determination.*

In an experiment with milk in the Hortvet apparatus the temperature fell from −0·55° to −1·6° C., *i.e.* a supercooling of 1·05° C., in 3·75 minutes. At this point freezing was started, and the temperature rose again to −0·55° C., the freezing point of the milk, in 1·25 minutes. If no ice had been present in the liquid, the loss of heat from the milk to the cooling medium during the latter period of 1·25 minutes would have corresponded with a lowering of

temperature of $1{\cdot}05 \times \frac{1{\cdot}25}{3{\cdot}75}$, or 0·35°. The loss of heat, however, is compensated by the formation of ice. The actual amount of ice formed is $\frac{0{\cdot}35}{80}$ grm. for every grm. of liquid present, that is to say, the milk has been concentrated by $\frac{0{\cdot}35}{80}$ths of its original volume. Therefore, in Equation II above, K′ becomes $\frac{0{\cdot}35}{80}$ or 0·0044.

(*b*) *Comparison of Hortvet's published results for sucrose solutions with those of Raoult, which are acknowledged to be the most accurate available.*

Hortvet gives −0·422° and −0·622° C. as the freezing points, respectively, of 7 and 10 grms. of sucrose in 100 ml. of solution. In Raoult's paper all sucrose solutions are in terms of grms. of sucrose to 100 grms. of water. I find, by weighing, that Hortvet's two test solutions correspond with 7·3373 and 10·6895 grms. of sucrose to 100 grms. of water. Applying Raoult's empirical formula, we find that the true freezing-point depression of Hortvet's 7 per cent. solution should be

$$\frac{18{\cdot}72 \times 7{\cdot}3373}{342 - (0{\cdot}99 \times 7{\cdot}3373)} = 0{\cdot}410^\circ.$$

Similarly, the true freezing-point depression of Hortvet's 10 per cent. solution should be 0·604° C.

Substituting these figures for C, and Hortvet's figures for C′ in Formula IV (above), we have

$$\text{(i)}\quad 410 = 422 - 422\,(K + K')$$
$$\text{and}\quad \text{(ii)}\quad 604 = 622 - 622\,(K + K'),$$

whence K + K′ = (i) 0·028; (ii) 0·029.
If we take K, the supercooling correction, for Hortvet's apparatus, as 0·017, K′ becomes 0·011 to 0·012.

(*c*) *Determination of the freezing point of a given sample of milk by Hortvet's method and by a fully corrected method, using, in both cases, the same thermometer, so that uncertainties in thermometer-calibration are eliminated.*

The freezing points of three different samples* of milk taken with the Hortvet apparatus, were found to be −0·535°, −0·534°, and −0·534°. The thermometer was changed over to the apparatus described below and the freezing points of the same three samples, corrected for supercooling, were found to be −0·522°, −0·520°, and −0·519°, respectively. Making the necessary substitutions in Formula IV, we have

$$\text{(i)}\quad 0{\cdot}522 = 0{\cdot}535 - 0{\cdot}535\,(K + K'),$$
$$\text{(ii)}\quad 0{\cdot}520 = 0{\cdot}534 - 0{\cdot}534\,(K + K'),$$
$$\text{(iii)}\quad 0{\cdot}519 = 0{\cdot}534 - 0{\cdot}534\,(K + K').$$

Whence K + K′ = (i) 0·024; (ii) 0·026; (iii) 0·028; the average being 0·026. If K is taken as 0·017, K′ is 0·009.

* These were ordinary samples bought from dairies in London. The first was bought on January 26th, 1933, from Dairy A, and the last two on February 14th, 1933, from Dairies A and B.

(*d*) *Direct determination of the heat-transference factor.*

If it were possible to remove the alcohol from the jacket of the Hortvet apparatus immediately before freezing starts, and thus isolate the milk, at the moment of freezing, from the influence of the surrounding medium, a direct measurement of the heat-transference factor could be obtained. This cannot be done in the Hortvet cryoscope, but is easily done in the apparatus described below. Determinations of the freezing point of different portions of the same sample of milk in this way gave the following figures:

	With removal of alcohol	Without removal of alcohol
	—0·5155°	—0·521°
	—0·515°	—0·519°
	—0·515°	—0·521°
		—0·5205°
		—0·5205°
		—0·520°
Average	—0·515°	—0·520°

The difference between these results, 0·005, corresponds with the term K′C′ in equation II above. Since C′ is 0·520, therefore K′ is 0·0096.

Of these four methods of arriving at the value of the heat-transference factor, the first is clearly very rough, and, almost certainly, gives too low a result. The second depends upon the assumption that Raoult's thermometer was correctly calibrated, a point upon which we have no definite information. The values for K′ found by the third and fourth methods are in close agreement. Although they have been determined with the aid of an apparatus differing in design from that of Hortvet, it is highly probable that they are applicable to Hortvet's cryoscope, and that 0·026 is a close approximation to the value of $K + K'$ in Equation IV. This implies that the apparent freezing point of milk, as determined by Hortvet's method, is 0·014° C. below the true freezing point, that is to say, his figure —0·550° C. corresponds with —0·536° C. for the true freezing point. It is of interest to note that in my report to the Local Government Board in 1914 I gave the average freezing point of 111 samples of milk from single cows as —0·5366°.

EFFECT OF INCOMPLETE STIRRING.—It has been stated by several observers that, in the Hortvet apparatus, variations in the amount of supercooling have practically no effect on the freezing point of milk. This may be due, I think, to the method of stirring adopted. If a solution of sucrose is partially frozen in the Hortvet apparatus, the inner tube then taken out, and the stirrer moved up and down, it is at once obvious that stirring is weak, and that the ice crystals are not thoroughly agitated and mixed with the liquid. It is not easy to stir a liquid properly with a round wire. A flat surface is required, with as large a superficial area as possible. The effects of incomplete stirring are more evident when supercooling is slight, and consequently the amount of ice in the liquid relatively small. The abstraction of heat by the cooling medium tends to lower the temperature of the liquid in the inner vessel, and stirring is not sufficiently vigorous to bring the small number of ice particles quickly into contact with all parts of the liquid. The result is that equalisation of temperature by the formation

of more ice is unduly delayed, and the observed freezing point is too low. Since this effect is more pronounced with small amounts of supercooling, the graph in Fig. 2 tends to become horizontal, thus giving the impression that supercooling has little or no influence upon the freezing point. I have found that the substitution of a wire loop stirrer for the flat stirrer in the apparatus described below, does actually have this effect. If, on the other hand, a really efficient form of stirrer is fitted to the Hortvet apparatus, heat interchange with the cooling medium through the alcohol in the jacket is accelerated, and it becomes difficult to get a steady reading of the thermometer. It would seem that in the Hortvet apparatus steadiness of temperature at the freezing point is secured mainly by a fortunate oversight in the matter of stirring. Whether or not this explanation is the true one, it is, in my experience, very difficult to get a satisfactory measurement of the supercooling correction K in Hortvet's apparatus.

DESCRIPTION OF NEW APPARATUS.—The freezing-point apparatus shown in Fig. 1 has been designed for the quick and accurate determination of the true freezing point of milk. With the exception of the thermometer and the two-way glass tap and tubing, no glass at all is used in its construction. All the parts have been made in my laboratory from brass sheet and tubing, and compressed cork, the metal joints being soldered.

The outer cylindrical vessel, A, and the removable cover, B, are made from 30-gauge brass sheet. The cover, B, overlaps the cylindrical side of A to a depth of about ½ inch and carried a central cylindrical vessel, C, made from 0·006-inch brass foil. From the lower end of this cylinder a tube, D, leads to the outside of the cover. The cover also carries two short tubes, E and F, open at both ends, a tube, G, closed at the lower end and a tube, H, ending in a perforated ring. The tubes are all made of "telescopic" brass tubing, E, F and G being of the grade known commercially as "3 best" (approximately 5/16 inch external diameter), and D and H of the grade known as "A best" (approximately 3/16 inch external diameter). The ring at the bottom of tube H carries about 10 holes made with a 1/16 inch twist drill. There is a free passage from the bottom of tube H into both arms of the ring. The freezing-tube J is made from 0·006-inch brass foil, joined to a narrow horizontal rim, L, made from 30-gauge brass sheet. I have also used freezing-tubes made of glass, but thin metal sheet has the advantage of more rapid temperature equalisation, and also of lower specific heat, and therefore a lower value for the supercooling correction. When the freezing-tube is placed in position in the vessel C there is a clearance of 2·5 to 3 mm. (3/32 to 1/8 inch) at the sides, and about 5 mm. at the base. This amount of clearance is important. It should not fall below 2·5 mm. Small studs on the outer surface of the freezing-tube, or preferably on the inner surface of the vessel C, serve to keep the freezing-tube in a central position, and maintain approximately the right clearance. The insulating casing, M, is built up from slabs of compressed cork. The ¾-inch slabs sold as bath-mats answer the purpose well. These are cut into squares with sides measuring about five inches, and holes are cut in the centre of each square of a diameter equal to that of the cylinder A. A sufficient number of these squares are then glued together under a heavy weight, care being taken that the holes are accurately placed one

above the other. The solid block of compressed cork thus obtained is trimmed with sandpaper, so that the brass cylinder A fits snugly into it. The upper inch or

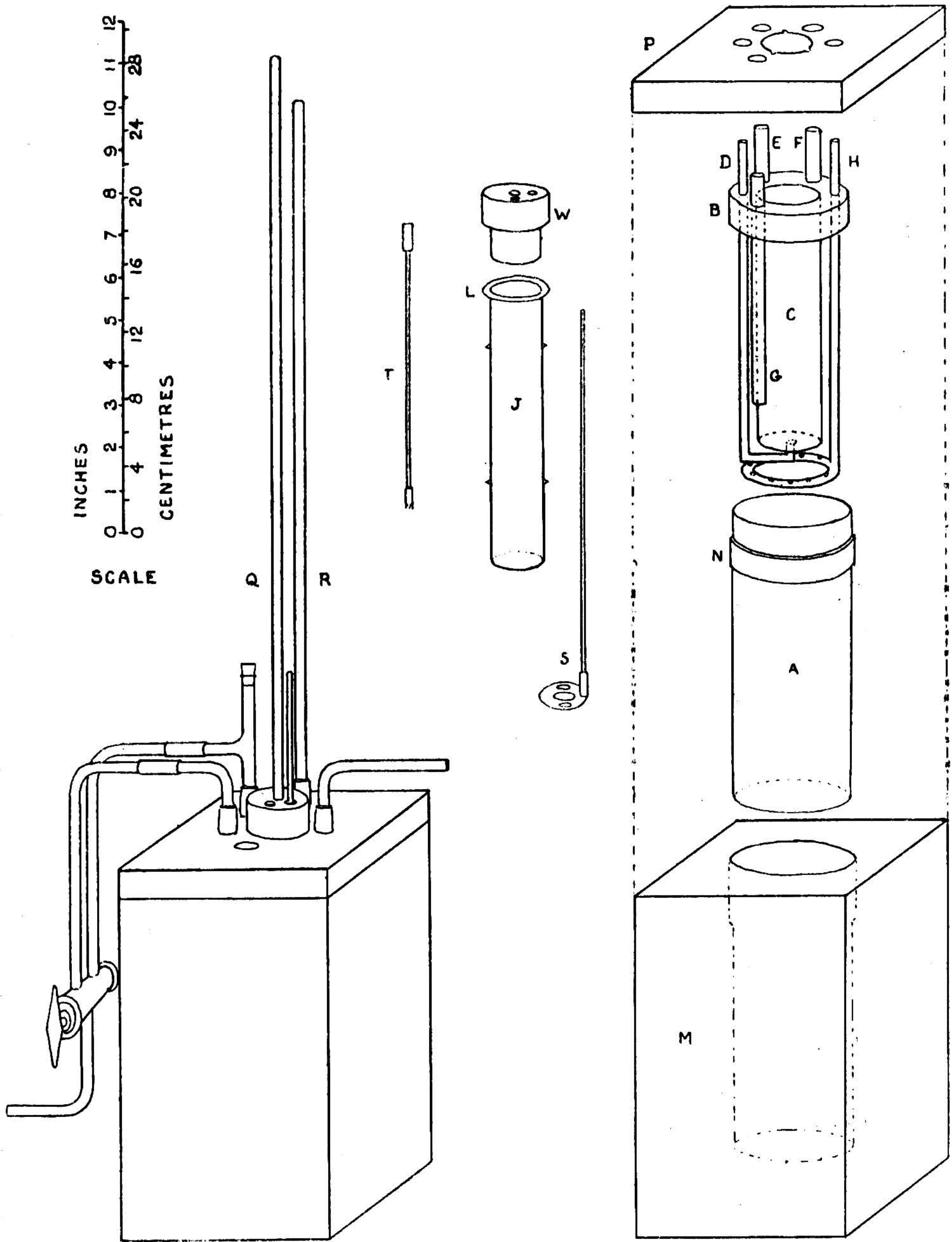

Fig. 1

so of the cork casing has a somewhat larger internal diameter so as to allow for the overlap of the cover and the rubber band N. The base is then formed by another 5-inch cork square in which no central hole has been cut. If the top of the cover B

is not flush with the top of the cork casing, it is raised by glueing cork discs to the required thickness on the floor of the casing. The insulating cover, P, is similarly made from a 5-inch square of compressed cork. It has a central hole slightly larger than the diameter of the freezing-tube J, but less than that of the rim L, and small notches are cut to allow of the passage of the studs on the outer surface of J. Holes are also cut to accommodate the various tubes projecting from the cover B. These holes are made large enough to take the rubber connections that are to be fitted over the tubes.

The freezing-tube J is fitted with a cork, W, of the shape shown in the drawing. This cork carries a central hole for the thermometer, Q, and holes for the rod of the stirrer and for the insertion of the starter. Care must be taken that the central hole is accurately bored so that the thermometer bulb is in the centre of the freezing-tube. The stirrer, S, is made from a disc of 30-gauge brass plate. It should move easily up and down in the freezing-tube, and the central hole should be large enough to clear the thermometer bulb easily. The two other smaller holes are intended to facilitate the passage of ice crystals and liquid during stirring. The stem of the stirrer is of non-conducting material. A No. 10 bone or composition knitting needle answers the purpose well. It is riveted into a short length of brass tube soldered to the stirring plate. The starter, T, is a length of 12-gauge brass rod, soldered at the lower end into a short piece of narrow brass tube. The open end of the tube is notched to facilitate extraction of small quantities of powdered ice from the bottom of the tube G.

To assemble the apparatus, the cover B is fitted on to the cylinder A, and the joint made air-tight with a wide rubber band or with adhesive tape. The cylinder is placed in position in the cork casing with the tube G to the front, and the cork cover put on. Tube H is connected by rubber tubing with a drying tower or sulphuric acid wash-bottle, and tubes D and E with a two-way tap leading to a water-pump. The connection on tube E is made with a glass T-piece to allow of the introduction of ether and also of a gauge tube when required. The cooling-bath thermometer, R, is held in the tube F by a short piece of rubber tubing. A few drops of water are introduced into the tube G to provide ice for starting.

METHOD.—To carry out a freezing-point determination, 400 ml. of ether are introduced through the tube E into the cylinder A by means of a funnel in the glass T-piece. The open end of the T-piece is tightly corked and air is drawn through the apparatus by the water-pump. The quicker the air current, the less time will it take for the temperature to fall. Sometimes it is possible greatly to increase the rate at which the temperature falls by using two water-pumps connected in parallel. Dilute alcohol (about 15 per cent.) sufficient in amount to fill the space between the vessels C and J to a depth of about three inches is poured into C. The amount necessary (about 25 ml.) should have been previously ascertained by trial. About 50 to 60 ml. of the sample, the freezing point of which is to be determined, are introduced into the freezing-tube J. The liquid should cover the bulb of the thermometer completely, the base of the bulb being well clear of the bottom of the vessel. The cork, fitted with stirrer and thermometer, is inserted, and the freezing-tube is placed in position in the apparatus. Stirring should be slow, about one up-and-down stroke every two or three seconds. The

ether bath should be taken down to about $-2°$ or $-3°$ C. When the temperature of the solution, as shown by the central thermometer, indicates the required amount of supercooling (normally about one degree), the two-way tap is turned, and the alcohol is rapidly sucked out from the space between C and J by the water-pump. If a small bottle is inserted between the two-way tap and the pump the alcohol can be recovered and used again. The tap is then turned back again to its former position. If the temperature of the ether falls too low, the air current can easily be regulated by partly closing the two-way tap. A reading of the thermometer is now taken, to obtain the amount of supercooling, and freezing is started by fragments of ice scratched out of the bottom of tube G by the notched end of the starter. The temperature rises quickly to the apparent freezing point. Stirring should be at the same slow rate, about one stroke every two or three seconds, and the thermometer should be tapped. During the tapping, stirring is temporarily stopped, the thermometer is firmly held by one hand, and, with a rubber-covered rod in the other hand, a rapid succession of sharp downward taps is given to the top end of the thermometer. In most freezing-point thermometers this causes the mercury meniscus to rise about 0·005° to 0·007°. Care must be taken not to let the base of the thermometer bulb come into contact with the floor of the freezing-tube, or serious errors may result. Tapping is repeated at intervals until it causes no further rise. It will be found that the final temperature is maintained steadily for several minutes.

It is occasionally found, especially when determining the freezing point of water or of sucrose solutions, that the liquid starts to freeze spontaneously when a certain degree of supercooling has been reached. If the two-way tap is turned immediately this happens, thus withdrawing the alcohol quickly from the space between the two vessels C and J, the final reading is not appreciably affected. One of the advantages of a metal freezing-vessel over a glass one is that spontaneous freezing, for some unexplained reason, is not so liable to occur.

Supercooling Correction.—Before proceeding to the routine examination of milk samples the supercooling correction should be determined. As already explained, the heat-transference factor K′ in Equation III has been practically eliminated by the method of construction of the apparatus, so that only the supercooling correction K has to be considered. For this purpose we determine the apparent freezing points of the same sample of milk for different amounts of supercooling, say, from half a degree to two degrees. A fresh portion of the sample should be used for each determination. The results are plotted on squared paper, and should lie in an approximately straight line (Fig. 2). The freezing point for supercooling nil can thus be found, and the supercooling correction calculated from Equation I above, which for this purpose can be written in the following form:

$$K = \frac{C' - C}{C'S}$$

As already mentioned, however, it is difficult to determine K accurately, and it is perhaps sufficient, for practical purposes, to dispense with this somewhat laborious operation, and to take the value of K as being 0·015 for milk. It is obvious that no supercooling correction is applicable to the freezing point of water, since the separation of ice cannot cause concentration of the liquid.

ADVANTAGES OF THE APPARATUS.—The main features of this apparatus are:—

(i) Heat exchange between the solution and the surrounding medium at the moment of freezing is practically eliminated.

(ii) The supercooling correction can be determined with sufficient accuracy.

(iii) The final temperature remains constant for several minutes.

(iv) Air is drawn through the ether instead of being driven through it, so that ether vapour does not tend to escape and pervade the room.

(v) No glass is used except in the thermometers and two-way tap, with a reduction in the risk of breakage.

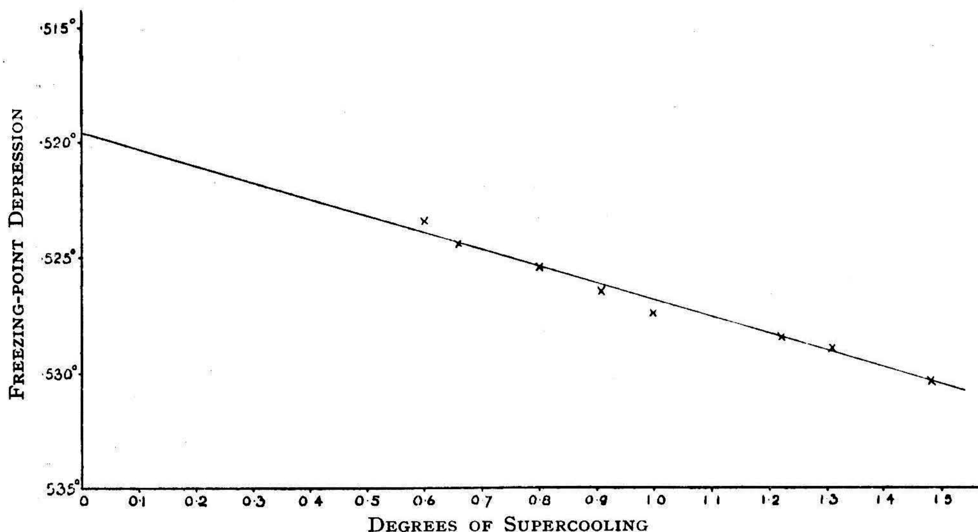

Fig. 2

Excellent heat insulation is secured by the compressed cork casing, and with a good water-pump the requisite low temperatures can be quickly reached.

THE THERMOMETER.—I have not dealt with the question of the thermometer, although this is perhaps the most important part of the apparatus. It is obvious that the expression "true freezing point" has no meaning unless the values are given in terms of an accurately calibrated thermometer. I am informed that the National Physical Laboratory, who have been working upon this subject at the request of the Empire Marketing Board, have now completed the installation of apparatus which will permit of the calibration of freezing-point thermometers with an accuracy of $\pm 0{\cdot}002°$ C.

It would be of advantage if the thermometer were graduated down to $-2{\cdot}5°$ C., to facilitate the determination of the supercooling correction.

I am informed by Messrs. Griffin & Tatlock, Ltd., Kemble Street, Kingsway, that they can make this apparatus at an approximate price of £4 10s. 0d., exclusive of thermometers.

A Note on the Composition of Some Fatty Materials Found in Ancient Egyptian Tombs

BY A. BANKS, PH.D., AND T. P. HILDITCH, D.SC., F.I.C.

(Read at the Meeting of the North of England Section, December 3, 1932)

AN examination has been made of four specimens of ancient Egyptian fats, which had been taken from graves of various dates from about 3000 to 1350 B.C., and were very kindly placed at our disposal by Mr. A. Lucas, O.B.E., F.I.C.

Fats of this nature have been examined on a few previous occasions. Lucas (*The Tomb of Tut-ankh-Amen*, Howard Carter, II, Appendix II, 176, 177; *J. Egyptian Archaeology*, 1930, **16**, 46, 47) refers to analyses made by Dr. R. Thomas, of Messrs. Lever Brothers, Ltd., who found that two fats from the tomb of Tut-ankh-Amen consisted chiefly of stearic and palmitic acids, with some corresponding glycerides. A. Chaston Chapman and H. J. Plenderleith (*J. Chem. Soc.*, 1926, 2614; Howard Carter, *loc. cit.*, Appendix IV, 206–210) investigated a cosmetic from a sealed jar in the same tomb; this contained 59·1 per cent. of fatty matter soluble in petroleum spirit and 28·6 per cent. of ether-soluble material, the latter consisting apparently of "oxidised" (hydroxylated) acids. These authors noted that the fatty matter, which was relatively saturated (iodine value, 4·5) and highly acid, possessed a smell resembling that of coconut, but the presence of oils of this type was not indicated by the Reichert (0·9) and Polenske (0·5) values. They concluded that the original cosmetic probably consisted of about 90 per cent. of a neutral animal fat with about 10 per cent. of some resin or balsam.

Our present work confirms and, to some extent, amplifies these former observations. In particular, we can identify the "coconut" odour, referred to by Chaston Chapman and Plenderleith, as being that characteristic of any unsaturated fat which has undergone disruptive oxidation into nonoic and azelaic acids or azelao-glycerides. Moreover, in the present series, evidence was also found of the presence, usually in small proportions, of azelaic and some other acids which had clearly resulted from slow oxidation of the unsaturated (oleic) portions of the original fats.

It will be convenient to record the observations made on each fat before drawing attention to some interesting features which they present.

(i) *Specimen from a Bowl in Pan Grave near Asiut, Upper Egypt; date, earlier than* 1580 B.C.—Sufficient of this material was available for a fairly comprehensive examination. It was in soft lumps of a cheese-like consistence, and was composed of about 66 per cent. of fatty matter, 24 per cent. of fibrous organic matter, 9 per cent. of ash, and 1 per cent. of moisture or volatile matter. The fibrous organic matter appeared to be of the nature of cellulose, and was probably derived from vegetable material* originally present with the fat, whilst the ash consisted, for the most part, of silica (sand).

* Petrie and Quibell (*Naquada and Ballas*, 1895, p. 39) similarly identified vegetable fibre in fat from an Egyptian jar, and concluded therefrom that the fat itself was of vegetable origin; but, as Chaston Chapman and Plenderleith (*loc. cit.*) point out, there is good authority for the belief that the Egyptians preserved fats by rolling them in vegetable fibre, so that the presence of the latter can hardly be accepted as evidence of the origin of the fat.

The fatty matter, which had been extracted with petroleum spirit (b.pt., 40–60° C.), was a hard, tallow-like substance, with a faint characteristic smell (definitely reminiscent of that of a fat after complete oxidation with potassium permanganate in acetone); it gave the following general analytical figures: saponification value, 201; acid value, 26·4; iodine value (Wijs), 3·5; acetyl value, 42·5. The fat (50 grms.) was saponified, and the resulting mixed fatty acids were converted into methyl esters which were fractionally distilled at about 0·5 mm. pressure, in order to ascertain their approximate composition. The aqueous liquor recovered from the saponification was neutralised and evaporated; the residue of sodium sulphate, etc., crystals was extracted with acetone and the acetone extract (3·5 grms.) distilled, when a viscous liquid (3 grms., b.pt., 126–130° C./0·1 mm.) was obtained which, on analysis by the acetin method, showed a content of 94 per cent. as glycerol.

The fractional distillation of the methyl esters (43·9 grms.) of the fatty acids led to quite normal results, except that the equivalent of the lowest-boiling fraction (2·53 grms.) was unusually low (206·7). Examination of the acids obtained from this fraction by hydrolysis disclosed only (i) a fatty acid sparingly soluble in alcohol, which melted at 60·5–61° C. (unaltered by admixture with palmitic acid), and (ii) a small amount of an acid which was extracted from the more soluble acid fractions by boiling with water; this melted at 95° C. alone, and at 100° C. when mixed with azelaic acid (m.pt., 104° C.). In other fractions of the distilled esters, palmitic and stearic (but no other saturated) acids were definitely identified. The small proportion of unsaturated acid was not definitely identified, but was assumed to be oleic acid, and the further assumption was made that the ester of lower equivalent than methyl palmitate was dimethyl azelate (equivalent 108). On this basis the composition of the mixed methyl esters was: azelate (1·7 per cent.), palmitate (35·8 per cent.), stearate (56·3 per cent.), oleate (3·8 per cent.), and unsaponifiable matter 2·4 per cent. The higher fatty acids present, therefore, were made up of a mixture of about 37 per cent. of palmitic, 59 per cent. of stearic, and 4 per cent. of oleic acid.

The acetyl value of the fat (42·5) and the mean equivalent of the higher fatty acids present (273, calculated from the fractionation analysis) correspond with mixtures of about equal proportions of triglycerides and diglycerides, or with about 84 per cent. of triglycerides and 16 per cent. of monoglycerides (or any values within these limits), but either corresponds with a content of about 20–25 per cent. of free fatty acid (as oleic), the observed figure being about 13 per cent. In other words, the observed acetyl value of the fat is high in comparison with the free fatty acid content. In a fat in which hydrolytic rancidity has set in under more usual circumstances (*e.g.* highly acid palm oils, *cf.* Hilditch and Jones, *J. Soc. Chem. Ind.*, 1931, **50**, 171T) the acetyl value is, on the contrary, almost invariably comparatively low compared with that calculated from the free acidity. This implies that, during rancidity changes, fats are, for the most part, hydrolysed completely to glycerol and fatty acids. If, therefore, we assume that the original changes in the present fat followed the normal course, it follows that a considerable amount of free fatty acid originally present must have disappeared. This would be consistent, as will appear later, with the observed low proportion of

oleic acid and the presence of traces of azelaic and other acids of low molecular weight.

(ii) *Specimen from a Pot near Asiut; Date, Fifth Dynasty, about* 2700 B.C.—This was of a more granular nature than the previous specimen, and appeared to consist of about 50 per cent. of fat, 12 per cent. of mineral, sandy matter, and 38 per cent. of non-fatty organic matter. As extracted by petroleum spirit, the fat was a hard tallow-like substance with saponification value 207, acid value 130, iodine value 2·8.

The mixed fatty acids obtained by hydrolysis of the fat were boiled with water several times (in the course of which a small amount of azelaic and, possibly, nonoic acids was removed), and then had a mean equivalent of 270. They were converted into methyl esters which (11·2 grms.), by means of fractional distillation, were found to be composed as follows: Palmitate (52·9 per cent.), stearate (38·5 per cent.), oleate (7·4 per cent.), and unsaponifiable matter (1·2 per cent.). The higher fatty acids present in the fat, therefore, consisted of palmitic (53 per cent.), stearic (39 per cent.), and oleic (8 per cent.).

Owing to the small amount available it was not possible to carry out any further investigation of this fat; but the data obtained indicated a general similarity to the previous specimen, especially the relatively small amount of oleic acid present and the evidence of residual acidic products of oxidation of the latter acid.

(iii) *Specimen of Uncertain Origin, but possibly of First Dynasty from Abydos; Date about* 3000 B.C.—This, again, was a very hard, gritty material and, in fact, consisted very largely of accompanying mineral matter (probably sand); it was especially interesting, however, in that it yielded larger amounts of apparent degradation (oxidation) products than the other specimens. Extraction with petroleum spirit (b.pt. 40–60° C.) yielded only 1·2 per cent. of a solid fat (saponification value 301, acid value 230); the corresponding mixed fatty acids, after boiling out with water several times, had a mean molecular weight of 242·5, and an iodine value of 3·8, and melted at 48–53° C. This melting-point was depressed on admixture with myristic acid, but raised to 55° C. by admixture with palmitic acid; and, although the amount available was too small for any detailed study, it may be concluded with some certainty that palmitic acid was one of the chief components.

Further extraction of the residual material with methylated ether removed a further 3·5 per cent. of semi-solid material of an acidic nature (mean equivalent 114), which was soluble in boiling water, from which a small quantity of liquid separated on cooling. The solution possessed the odour of nonoic acid and, after removal of the separated liquid and further concentration, deposited a solid which melted indefinitely at 155–160° C. The whole of the material was then recovered from the aqueous solution, and crystallised from chloroform. The portion soluble in cold chloroform was recovered, and then recrystallised, when a small amount of impure azelaic acid (m.pt. 95° C., mixed with pure azelaic acid, 96° C.) was obtained. The greater part of the material, which had separated from the cold chloroform solution, was crystallised once from water and then melted sharply at 180° C. (mixed with succinic acid, m.pt. 181° C.; equivalent: found 60·3, calculated for $C_4H_6O_4$ 59).

There appeared to be more succinic acid than higher fatty acids or azelaic acid in this particular specimen; and, although it is conceivable that succinic acid might be found in place of, or with, azelaic acid in the oxidation products of a fish oil which originally would have contained clupanodonic acid (*cf.* Tsujimoto, *Bull. Chem. Soc. Japan*, **1928**, **3**, 299), it seems more likely that the presence of this acid is to be connected with that of some other non-fatty compound (probably a resin) in the original material.

(iv) *Specimen from a Perfume Vase in a Tomb in the Temple of Pepi II at Dashour; Date, Eighteenth Dynasty,* 1580—1350 B.C.—This was a very small sample of a soft, black, resinous material (9·5 grms.) which yielded the following extracts of soft, yellowish, grease-like material when extracted successively with: Petroleum spirit (b.pt. 40–60°), 1·0; methylated ether, 2·4; benzene, 0·1 grms.

The residue (6 grms.) was a hard, brittle resin, mainly organic in nature, but insoluble in the solvents employed; it was not further examined.

The various extracts, which were not dissimilar in appearance, were united for further examination (saponification value 446, acid value 372), and were boiled out several times with water, from which, after recrystallisation from dilute methyl alcohol, crystals of still impure azelaic acid were obtained (m.pt. 93–95° C., mixed with azelaic acid, 95–96° C.). The higher fatty acids (mean molecular weight 223, iodine value 7·0), from which azelaic and lower fatty acids had been removed as far as possible by solution in boiling water, yielded, on crystallisation from alcohol, a less soluble fraction, which melted at 56–57° C., whilst the portion which remained in solution also melted at this temperature. So far as could be judged from these, the only possible observations on the small amount of material, the higher fatty acids were again mainly palmitic acid (still contaminated to some extent with acids of low molecular weight); but the possibility was not entirely excluded that in this specimen, fatty acids, such as lauric or myristic, might also have been present.

GENERAL DISCUSSION.—The most interesting features of the fats examined would seem to be (i) the fact that glycerides are often still present after the lapse of 3000–5000 years, (ii) the relatively small proportions of oleic acid observed, and (iii) the invariable evidence of the normal oxidation scission products of oleic acid (azelaic and nonoic acids).

As regards the saturated acids, which were still apparently mainly intact, it is of interest to note that both palmitic and stearic acids are present in important amounts in the two fats of which we had sufficient for a detailed examination. The presence of stearic acid in quantity is not consistent with the original fat having been of vegetable origin, unless it came from a somewhat small group of genera included in the *Guttiferae* (e.g. *Allanblackia*), the *Sapotaceae* (*e.g.* shea butter) and a few other families (to which belong, for example, cacao butter and Borneo tallow). These are not likely, in the circumstances,* and the only other possibility of such a mixture of saturated fatty acids emanating from a vegetable

* Castor oil is believed to have been a frequent constituent of ancient Egyptian cosmetics, but no sign of it has been encountered in the present work. In any case, being a mixture of almost completely unsaturated glycerides, it would, if originally present, probably have completely disappeared by the same agencies which have led to the disappearance of most of the oleic acid.

fat would be from an originally unsaturated fatty oil containing relatively small amounts of palmitic and stearic acids; this, however, would involve the disappearance of most of the oil by oxidation, and it is unlikely that, in this case, so high a proportion of almost-saturated glycerides of comparatively low acetyl value would result. On the other hand, the proportions of palmitic and stearic acids, although widely different in the two fats which we were able to study in detail, fall well within the possible limits for an animal depôt-fat (tallow), and it therefore looks as though the most likely origin of these two specimens, at all events, was the body fat of some animal, quite probably an ox. Unfortunately we were not able to obtain any additional evidence on this point from examination of the unsaponifiable matter in the fat.* In the other fats, of which only very small quantities were available, palmitic acid was equally in evidence, and, although we have not sufficient data to be at all positive, it seems quite probable that these were of the same general nature as the former; as mentioned above, however, it is also possible that the fat from the perfume vase may have contained definite amounts of a saturated acid of lower molecular weight than palmitic acid.

Unless we assume that fat-hydrogenation was an art known to the Egyptians, we are confronted with the fact that, since any natural fat known to contain palmitic and stearic acids in the observed ratios also contains oleic acid in at least equal proportions to either of these, combined oleic acid originally present must have disappeared to a large extent. The manner of its disappearance appears fairly obvious. Atmospheric oxygen has slowly attacked the oleic radicals and eventually nonoic acid and azelao-glycerides have been produced; the latter are comparatively easily hydrolysed into free azelaic acid and di- or mono-glycerides, as the case may be. More drastic oxidation changes may have, of course, ensued; but, apart from these, it is probable that, in the course of centuries, both nonoic and azelaic acids have largely disappeared by slow evaporation. This is suggested by the fact that nonoic acid was positively recognised only by its characteristic odour, whereas the relatively still less volatile azelaic acid was still present in quantities sufficient for isolation in a comparatively pure state. It is not without interest to find that atmospheric oxidation of mixed saturated-unsaturated glycerides over an extreme length of time (3000—5000 years) follows apparently much the same course, and yields the same products, as an oxidation conducted in the course of a few hours by means of potassium permanganate or similar chemical reagents under suitable conditions.

It is a pleasure to acknowledge the assistance given us by Mr. Lucas, not only in providing the material for this study, but also in the presentation of the results.

THE UNIVERSITY,
LIVERPOOL

* Chaston Chapman and Plenderleith (*loc. cit.*) also failed to detect cholesterol, phytosterol or other similar crystalline substance in the unsaponifiable fraction, and point out that this is not altogether surprising.

The Quantitative Separation of Aluminium from Iron

BY J. HASLAM, M.SC., A.I.C.

(*Read at the Meeting of the North of England Section, October* 15, 1932)

A SHORT time ago the question arose in our laboratory as to the best method of determining aluminium in an iron-aluminium alloy containing about 14 per cent. of aluminium.

Of the various methods of separation of iron from aluminium which have been proposed, we decided to adopt that depending on the precipitation of the iron as ferrous sulphide in ammoniacal tartrate solution.

The next question was the best method of recovering the aluminium from the ammoniacal tartrate filtrate obtained after removal of the iron.

Treadwell and Hall (*Quantitative Analysis*, 7th Ed., p. 109) suggest that the filtrate should be evaporated to dryness with the addition of a little sodium carbonate and potassium nitrate, and the residue, after gentle ignition in a porcelain dish to destroy the tartrate, dissolved in dilute nitric acid, the carbon filtered off, and the aluminium precipitated as hydroxide by the addition of ammonia.

Hillebrand and Lundell (*Applied Inorganic Analysis*, 1929, p. 61) remove the tartaric acid from the ammoniacal tartrate filtrate by wet oxidation with sulphuric and nitric acids, finally precipitating the aluminium as hydroxide by the addition of ammonia.

Both these methods of destruction of tartaric acid are tedious, and care must be taken that all traces of organic matter are removed before proceeding to the precipitation of the aluminium as hydroxide.

Schoeller and Webb (ANALYST, 1929, **54**, 711) precipitate the aluminium directly as an aluminium tannin complex in the ammoniacal tartrate filtrate from the separation of the iron; this complex is then filtered off, ignited, purified and weighed.

The aluminium tannin complex thus obtained is very bulky and, although we have found that it is possible to work with an amount of aluminium tannin complex corresponding with 0·025 grm. of Al_2O_3 by using a platinum cone support for the filter-paper in the filtration, the ignited tannin complex is always impure, and the weight of the purified oxide is usually about 0·0004 grm. below the theoretical weight.

In our own method, which we have investigated by analysis of solutions containing known amounts of iron and aluminium, and which is fully outlined on p. 271, the iron is precipitated as sulphide in ammoniacal tartrate solution, and,

after removal of sulphides, etc. from the filtrate, the aluminium is precipitated with 8-hydroxyquinoline.*

The method is reasonably rapid and the results obtained are very satisfactory, as is shown on p. 272.

SOLUTIONS USED.—(i) *Standard Ferric Solution.*—Fourteen grms. of ferrous ammonium sulphate (B.D.H.) were treated in a conical flask with about 20 ml. of distilled water, 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid, and the mixture was evaporated on the sand-bath until of syrupy consistence. The evaporation was repeated with a further 10 ml. of concentrated hydrochloric acid, the residue was dissolved, and the solution diluted to one litre with distilled water.

(ii) *Standard Aluminium Solution.*—The aluminium metal used in the preparation of this solution contained:—Silicon, 0·16; iron, 0·38; and manganese, 0·0024 per cent., as impurities.

The metal (1·0259 grm.) was dissolved on the water-bath in a mixture of 10 ml. of distilled water and 15 ml. of concentrated hydrochloric acid, the solution was diluted and filtered, and the filtrate was made up to a litre with distilled water.

By precipitation with 8-hydroxyquinoline, and deduction of the weight of iron hydroxyquinolate (due to the small amount of iron in the sample), it was found that one ml. of the above solution contained aluminium equivalent to 0·001926 grm. of Al_2O_3.

(iii) *8-Hydroxyquinoline Sulphate Solution.*—Five grms. of 8-hydroxyquinoline sulphate (B.D.H.) were dissolved in 100 ml. of distilled water.

(iv) *Ammonium Sulphide-Tartrate Wash-water.*—A solution of 2 grms. of tartaric acid (B.D.H.) in 400 ml. of distilled water was saturated with hydrogen sulphide, and the saturated solution was treated with about 5·5 ml. of concentrated ammonia solution.

METHOD.—To 50 ml. of the standard ferric solution (= 0·1 grm. of iron) in a 200-ml. beaker, were added 2 grms. of tartaric acid and a known amount of the standard aluminium solution. The solution was heated to boiling, and a current of hydrogen sulphide was passed through it for ten minutes, after which about

* The method of precipitation of the aluminium is essentially that of Berg (*Z. anal. Chem.*, 1927, **71**, 369), who has made extensive use of 8-hydroxyquinoline for the precipitation of metals generally.

The most important gravimetric methods suggested by him up to the present date are as follows:—

Copper ..	*Z. anal. Chem.*,	1927, **70**, 341;	ANALYST, 1927, **52**, 302.
Magnesium ..	,, ,,	1927, **71**, 23;	,, 1927, **52**, 431.
Zinc	,, ,,	1927, **71**, 171;	,, 1927, **52**, 494.
Cadmium ..	,, ,,	1927, **71**, 321;	,, 1927, **52**, 611.
Aluminium ..	,, ,,	1927, **71**, 369;	,, 1927, **52**, 611.
Bismuth ..	,, ,,	1927, **72**, 177;	,, 1928, **53**, 58.
Cobalt	,, ,,	1929, **76**, 191.	
Iron	,, ,,	1929, **76**, 191.	
Manganese ..	,, ,,	1929, **76**, 191.	
Nickel	,, ,,	1929, **76**, 191.	
Titanium ..	,, ,,	1930, **81**, 1;	,, 1930, **58**, 596.

Since this paper was completed my attention has been drawn to a paper by E. Jung (*Z. Pflanz. Düng.*, 1932, **26A**, 1–8; *B.C.A.*, B, 1932, **51**, 1129), in which is recorded a satisfactory adaptation of the method of determining aluminium by means of 8-hydroxyquinoline in soils and silicates containing iron and titanium.

5·5 ml. of concentrated ammonia solution were added, and the mixture was heated on a boiling water-bath for twenty minutes. The current of hydrogen sulphide was then continued for five minutes, and, after the addition of 1·5 ml. of concentrated ammonia solution, the mixture allowed to settle.

The precipitate was filtered off on a No. 41 Whatman filter-paper (15 cm.), and washed five times with the ammonium sulphide tartrate wash-water. The filtrate and washings were heated to boiling; after the liquid had been boiled for about 10 minutes a precipitate of sulphur was obtained, but this disappeared on further heating, and finally a perfectly clear liquid was obtained.

Ten ml. of concentrated hydrochloric acid and one drop of methyl orange solution were next added to this clear liquid (about 200 ml.), followed by the concentrated ammonia solution, drop by drop, until the liquid was pale yellow in colour, after which a further 2·5 ml. of concentrated ammonia solution were added, and the solution was diluted to about 350 ml. with distilled water.

Hydroxyquinoline sulphate solution was added, drop by drop, with constant stirring, to this ammoniacal solution until the supernatant liquor was distinctly yellow, after which an excess of 5 ml. was added. The liquid was heated to 90° C. and stirred to coagulate the precipitate, and, after standing for about four hours, or overnight, the aluminium hydroxyquinolate was filtered off on a weighed Gooch crucible, washed well with warm water, dried at 140° C. for one hour, and weighed.

This experiment was repeated with different amounts of the standard aluminium solution, and the results obtained are given below:

	Iron. Grm.	Alumina added Grm.	Alumina found Grm.
(i)	0·1	0·0289	0·0288
(ii)	0·1	0·0241	0·0242
(iii)	0·1	0·0194	0·0194
(iv)	0·1	0·0144	0·0145
(v)	0·1	0·0096	0·0095
(vi)	0·1	0·0048	0·0048

I wish to express my thanks to the directors of Imperial Chemical Industries Limited for permission to publish this work, which was carried out in the Research Laboratory of their subsidiary company, I.C.I. (Alkali) Limited, Northwich.

A Milk Calculation Formula for use at Tropical Temperatures

By HERBERT HAWLEY, M.Sc., F.I.C.

Although Richmond's milk-calculation formulae are extremely valuable in temperate climates, they are of very little use at tropical temperatures. This is accounted for by the fact that the coefficient of expansion of milk of low gravity is very different according to whether the milk is watered or contains an excess of fat. For tropical countries it is necessary to devise a formula based on a higher

temperature than 60° F., so that the corrections involved in adjusting to the standard temperature will be small.

The formula below is based on the specific gravity of milk (weighed in air) held by a glass vessel at 85° F., compared with the weight of water held by the same vessel at 60° F. A hydrometer to give this gravity could easily be prepared, but, in practice, all gravities are determined by weighing in a 50-grm. Warden specific gravity bottle. These are hole-in-the-stopper bottles with glass caps to prevent evaporation. If these bottles are carefully calibrated and a table or simple formula made, to give the specific gravity directly by inspection from the weight of the bottle filled with milk, and if weighings are carried out to the nearest 5 mgrms., gravities take little, if any, longer to determine than with a hydrometer, and are of course reliable to the fourth place of decimals (the first decimal place of milk degrees). The formula has been calculated in the form used by Richmond in his *Dairy Chemistry* by the method of least squares from 18 determinations of fat, solids and specific gravity. Since then it has been tried on many hundreds of milks. It works equally well for Madras cow and buffalo milk, and usually gives a result accurate to 0·2 per cent. of solids-not-fat. Errors exceeding 0·2 per cent. are almost invariably associated with milks containing a large proportion of added water. The formula is:

$$\text{S.N.F.} = 0{\cdot}2872\,\frac{G}{D} + 0{\cdot}328\,F,$$

where S.N.F. represents the percentage of solids-not-fat; F, the percentage of milk-fat; D, the gravity at 85° F./60° F. glass in air; G, 1000D–1000.

The tables below have been calculated from this formula. To obtain the percentage of solids-not-fat in a sample of milk of which fat and specific gravity have been determined, all that is necessary is to add together the appropriate figures given in the two tables.

VALUE OF $0{\cdot}2872\,\frac{G}{D}$

Gr.	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
10	2·84	2·87	2·90	2·92	2·95	2·98	3·01	3·04	3·06	3·09
11	3·12	3·15	3·18	3·21	3·24	3·27	3·29	3·32	3·35	3·38
12	3·41	3·44	3·46	3·49	3·52	3·54	3·57	3·60	3·63	3·65
13	3·68	3·71	3·74	3·76	3·79	3·82	3·85	3·88	3·90	3·93
14	3·96	3·99	4·02	4·04	4·07	4·10	4·13	4·16	4·18	4·21
15	4·24	4·27	4·30	4·32	4·35	4·38	4·41	4·44	4·46	4·49
16	4·52	4·55	4·58	4·60	4·63	4·66	4·69	4·72	4·74	4·77
17	4·80	4·83	4·86	4·88	4·91	4·94	4·97	5·00	5·02	5·05
18	5·08	5·11	5·14	5·16	5·19	5·22	5·25	5·28	5·30	5·33
19	5·36	5·39	5·41	5·44	5·47	5·49	5·52	5·54	5·57	5·60
20	5·63	5·66	5·69	5·71	5·74	5·77	5·80	5·83	5·85	5·88
21	5·91	5·94	5·97	5·99	6·02	6·05	6·08	6·11	6·13	6·16
22	6·19	6·22	6·25	6·27	6·30	6·32	6·35	6·38	6·40	6·43
23	6·46	6·49	6·51	6·54	6·56	6·59	6·62	6·65	6·67	6·70
24	6·73	6·76	6·79	6·81	6·84	6·87	6·90	6·93	6·95	6·98
25	7·01	7·04	7·06	7·09	7·11	7·14	7·17	7·20	7·22	7·25
26	7·28	7·31	7·34	7·36	7·39	7·42	7·45	7·47	7·50	7·52
27	7·55	7·58	7·60	7·63	7·66	7·69	7·72	7·74	7·77	7·79
28	7·82	7·85	7·88	7·90	7·93	7·96	7·99	8·02	8·04	8·07
29	8·10	8·13	8·15	8·18	8·21	8·23	8·26	8·29	8·31	8·34
30	8·37	8·40	8·42	8·45	8·48	8·50	8·53	8·56	8·58	8·61

Percentage of fat	Value of 0·328 F.									
	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0	0	0·03	0·07	0·10	0·13	0·16	0·20	0·23	0·26	0·30
1	0·33	0·36	0·39	0·43	0·46	0·49	0·52	0·56	0·59	0·62
2	0·66	0·69	0·72	0·75	0·79	0·82	0·85	0·89	0·92	0·95
3	0·98	1·01	1·05	1·08	1·11	1·15	1·18	1·21	1·25	1·28
4	1·31	1·34	1·38	1·41	1·44	1·47	1·51	1·54	1·57	1·61
5	1·64	1·67	1·70	1·74	1·77	1·80	1·84	1·87	1·90	1·93
6	1·97	2·00	2·03	2·06	2·10	2·13	2·16	2·20	2·23	2·26
7	2·30	2·33	2·36	2·39	2·43	2·46	2·49	2·53	2·56	2·59
8	2·62	2·66	2·69	2·72	2·76	2·79	2·82	2·86	2·89	2·92
9	2·95	2·99	3·02	3·05	3·09	3·12	3·15	3·18	3·22	3·25
10	3·28	3·31	3·35	3·38	3·41	3·45	3·48	3·51	3·54	3·57
11	3·61	3·64	3·67	3·71	3·74	3·77	3·81	3·84	3·87	3·91
12	3·94	3·97	4·00	4·04	4·07	4·10	4·14	4·17	4·20	4·23

Public Analyst's Laboratory,
King's Institute, Guindy, Madras

Notes

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

ESTIMATION OF THE EXTRACT OF COFFEE AND CHICORY

On page 708 of The Analyst for November last a note appeared from Mr. E. H. Bunce, of Burma, giving results which had led him to the conclusion that Indian coffee yields a higher proportion of water-soluble extract than is usually attributed to genuine coffee, *viz.* 28 per cent. as against "the generally accepted figure of 24·0 per cent. for genuine samples." Mr. Bunce did not in his note describe his method of estimation of the extract, and there was an editorial interpolation in Mr. Bunce's note of the parenthetical sentence: "(*cf.* E. W. T. Jones in Johnston's *Analyst's Laboratory Companion*, 1920, p. 157, who, however, used a less complete extract.)"

Mr. Bunce has since written to explain that the method he used was the method of Jones referred to in the editorial sentence just quoted, and pointing out that the method appears in other text-books, especially mentioning Messrs. Moor and Partridge's *Aids to the Analysis of Food and Drugs.* It may be added that the method of Jones is also quoted in Mr. Parry's *Analysis of Food and Drugs*, and in Dr. Cox's more recent *Chemical Analysis of Foods*, though Dr. Cox, in describing Jones's method, gives a warning that, although Jones, for the interpretation of results, assumes the figure of 24 per cent. for the extract, yet "some pure coffees give an extract as high as 26 or 27 per cent."

I venture to suggest that the explanation of Mr. Bunce's conclusion that Indian coffee yields exceptionally more extract than is indicated in the formula of Jones may be merely that he has been more successful than was Jones himself in his application of the method which Jones put forward.

As long ago as 1882, subsequently to the description of Jones's method, the late Mr. Alfred Smetham proposed as an alternative method to either that of Jones or to the better-known and much earlier density method of Graham, Stenhouse and Campbell, the simple method of exhaustively extracting a weighed

portion of the dried coffee by repeated boiling and weighing the undissolved matter, taking the "extract" by difference. This method has been used in my own laboratory during the last fifty years on a great number of samples of coffee that have probably represented every source of supply ground in England, and the water-soluble matter thus determined in genuine coffee has never fallen to anything like the 24 per cent. assumed in the formula associated with the method of Jones. It usually approximates more nearly to the 28 per cent. now indicated by Mr. Bunce for Indian coffee.

It would now be interesting if Mr. Bunce would apply the method of Smetham, as he must have used it or seen it used in the days when I had the pleasure of counting him among my own assistants, and see whether he finds, as I expect he will, that it yields much the same average of 28 per cent. as he finds in his own application of the method of Jones.

The method of operation is to take 3 grms. of the dried coffee, boil for 10 minutes with 125 c.c. of distilled water, filter the liquor, wash back the insoluble matter into the beaker, and boil again with a similar quantity of water, repeating the process up to a fourth boiling, when the insoluble matter is collected on counter-poised filters, washed with hot water, dried and weighed.

Looking back at the last twenty-five samples of genuine coffee dealt with, I find that they gave, calculated on the dried coffee, an average of 70·9 of insoluble matter, indicating an average of 29·1 per cent. of soluble extract. Among these samples there were two giving 69 per cent. of insoluble and one giving 73 per cent., the rest varying from 70 to 72 per cent. This range is corroborative of the general experience of fifty years.

Although I have never previously used the method of Jones, in view of Mr. Bunce's communication, I have had it tried on three samples of coffee that happened to be under recent examination. Two of them (A and B) were, as received, rather coarsely ground; one (C) was, as received, more finely ground.

Coffee dried at 100° C.	"A"	"B"	"C"
Insoluble matter	72·4	71·3	70·9
Soluble extract (by difference) ..	27·6	28·7	29·1
	100·0	100·0	100·0
Method of Jones.			
Soluble extract: Operator J ..	21·6 22·4	22·8	24·4
Operator M ..	23·7 24·2	24·0	25·9

Both operators endeavoured to adhere to the instructions for the Jones's method, and the differences illustrate the liability to personal variation with a method that is empirical and not exhaustive. The nearer approach to full extraction by one of the operators in the case of sample C probably illustrates the effect of finer grinding. Did Mr. Bunce perhaps grind his samples still a little finer? and was this why, although using the method of Jones, he got a nearer approach to the normal quantity of soluble matter obtainable by exhaustive boiling?

17, Great Tower Street,
London, E.C.

Bernard Dyer

SUPPOSED POISONING BY TEA

As Public Analysts we had recently to investigate a fatal case which was thought at first to have been caused by poisoned tea, as the deceased was taken ill soon after drinking the tea, which differed widely in appearance from that which it had when freshly made.

The deceased was a railwayman, 66 years of age, who went to work about midday, taking with him, as usual, a bottle of strong tea containing sugar, but no milk, which when he left was still hot and was perfectly bright and clear. During that afternoon he drank a cup of this tea, and soon afterwards felt unwell, and he returned to his home very ill at 12·30 a.m. the next day, bringing with him the bottle containing the rest of the tea, which was then seen to be milky, and to contain a yellowish deposit.

This man was treated at his home by his doctor, but becoming worse, he was removed to the Infirmary, where he died thirteen days after he was first taken ill.

As no cause for this man's illness could be found, the organs and the tea were sent to us for analysis. The pathologist sent us all the principal organs, and some muscle, bone, urine, hair, skin, and the finger nails; he sent the stomach, large and small intestines unopened, requesting us to empty them of their contents and return the organs to him for examination, which was done. We examined all the specimens submitted to us, but could find no poison of any kind.

The rest of the tea brought home by the sick man was no longer clear, as it was when he left his house, but looked milky, although no milk had been put in it, and it contained a yellow sediment; for these reasons and from the fact that he was taken ill soon after taking the tea, his illness and death were thought to have been caused by the tea, to which some poisonous substance must have been added.

On heating this tea we found that it became almost perfectly clear and transparent, and then had the appearance of a strong infusion of tea; on cooling, it again became milky, and deposited the yellowish precipitate, and these changes on heating and cooling could be repeated indefinitely. The yellow precipitate we found to consist of caffeine and tannin, and to these natural constituents the milkiness and sediment were due. Nevertheless, the infusion was examined, but no added material was found besides sugar.

The cause of the death of this man was found in the small intestine, which was obstructed by large growths, which were found after we had emptied it and returned it for examination.

We wish to redirect attention to the fact that tea infusions, even when only moderately strong, do, on cooling, deposit caffeine and tannin, which is a matter of importance when determining these constituents, and has been lost sight of in many modern works dealing with the analysis of teas, in some of which directions are given to filter the infusions when cold, whereby parts of the caffeine and tannin are removed and low results for them obtained.

Dr. James Bell, in his *Analysis and Adulteration of Foods*, Part I, p. 28, published in 1881, specially directs attention to this risk, in the following words: ". . . and filtered hot to prevent deposition of the tannate of theine."

On the other hand, on pp. 340 and 341 of the *Official Methods of Analysis of the American Association of Official Agricultural Chemists*, published in 1925, filtration of the cold infusion is directed, which we have found yields low results for the caffeine and tannin.

J. T. Dunn
H. Charles L. Bloxam

AMYL ALCOHOL FOR MILK TESTING

The note by Mr. J. Houston in the Analyst (1933, p. 151) gives a timely warning of the need for care in the selection of amyl alcohol for the Gerber fat-test of samples of milk.

The comparative Gerber test with each fresh consignment is certainly necessary, preferably against gravimetric results (Röse–Gottlieb), on the same sample of milk, or, failing this, in comparison with a control in which a proved, satisfactory sample of amyl alcohol is used.

It appears, however, that the ten samples cited by Mr. Houston have a lower boiling point than consignments which are readily available in England.

The amyl alcohol which we are using at the National Institute for Research in Dairying, when distilled with an efficient fractionating column, 16 inches in length, yields a distillate of 92·4 per cent. of the volume between 136·8° C. and 137·8° C. This approximates to the boiling point of normal amyl alcohol, $CH_3(CH_2)_3CH_2OH$, (b.pt. 137° C. at 760 mm.). It differs from the ten samples from Northern Ireland, which are all of lower range of b.pt. (122° C.–135° C.). Our amyl alcohol gives Gerber-tests with milk which agree with the Röse–Gottlieb results within the limits of error of the method. The first small fraction which begins to come over at 126·8° C., as also the residue of this amyl alcohol, does not give enhanced readings when used for the Gerber test with milk.

On the other hand, my attention has been called to another type of "amyl alcohol," which consistently gave fat-percentages 0·1 per cent. too high when used in the Gerber butyrometers.

The undesirable impurity was concentrated in the residue (3·4 per cent. of the volume), which gave fat-results 0·6 per cent. too high. The last two fractions (137° C.–138° C., 66 per cent. of the volume, and 138° C. to 138·2° C., 4·4 per cent. of the volume), gave results for fat 0·1 and 0·2 per cent. too high, respectively. Earlier fractions (129° C. to 137° C.) were free from the impurity.

It seems that a guarantee of suitability for use in the Gerber apparatus should be required when supplies are purchased for this purpose, and that the claims of an amyl alcohol having a b.pt. of 137° C. should be considered.

JOHN GOLDING

NATIONAL INSTITUTE FOR RESEARCH IN DAIRYING,
SHINFIELD, NEAR READING

SPECIFICATION FOR AMYL ALCOHOL FOR USE IN THE GERBER TEST

THE reagent originally recommended by Gerber was simply amyl alcohol, but, in 1895, amyl alcohol with a range of 0·82 to 0·86 in sp.gr. at 15·6° C., and of 124° to 130° C. in boiling-point, was specified, and, a few years later, this was altered to:

Density at 15° C. ..	0·815
Boiling-point	128 to 130° C.
Colour	water—clear.

Special test:—One c.c. of alcohol + 11 c.c. of water + 10 c.c. of sulphuric acid (sp.gr. 1·820 to 1·825); shaken; centrifuged for 2 to 3 minutes, and left for 24 hours, gives no oily layer.

Recently there appears to have arisen a recurrence of the difficulty, found 30 years ago, that some samples of amyl alcohol satisfying Gerber's specification give high results in the milk test.

J. van Haarst (*Z. angew. Chem.*, 1903, 451) found that a sample of alcohol satisfying Gerber's specification gave fat results 0·60 to 0·95 per cent. too high; but alcohol of sp.gr. 0·820 and a dark yellow fusel oil of sp.gr. 0·845 gave good results, whilst the best quality of amyl alcohol was unsuitable for the test.

M. Siegfeld (*Z. angew. Chem.*, 1903, 1217–1220) also found results 0·9 to 1·0 per cent. too high when using the specified amyl alcohol, and stated that under the conditions of the Gerber test with water and acid, dehydration and oxidation of the amyl alcohol occur with the formation of insoluble or difficulty soluble products. These products are not produced in quantity sufficient for their actual

separation from the liquid, unless the temperature is raised above 60 to 70° C., but, although, at this temperature specified by Gerber, no actual separation occurs on heating for hours, fat, if present, is capable of extracting them, and, after long heating, the fat-result is high. The increase can be shown by heating the tubes after a test and re-centrifuging.

He recommended that, since Gerber's special test, with water, did not disclose the faulty character of a sample, a new stock of amyl alcohol should be compared in a test with milk against a reliable sample, and he stated that Gerber's requirements are immaterial. This test is now included in German descriptions of the Gerber test.

It is to be noted that the layer of "fat" separated during a test with satisfactory amyl alcohol is not by any means a clean separation of the fat of the milk. Droop Richmond (ANALYST, 1905, **30**, 326) showed that during the test the original fat of the milk was broken up, 0·3 per cent. of soluble acid (butyric, etc.) was lost, about 6 per cent. of the glycerides were hydrolysed into free fatty acids and glycerol, 18 per cent. were converted into amyl esters, and about 40 per cent. into diglycerides; a small amount of combined sulphuric acid, probably as sulpho-oleic, was present, and there was an increase in volume and in weight of about 3 per cent. The increase in volume due to formation of amyl esters, however, appears to compensate with a fair degree of accuracy for the loss of glycerol and butyric acid. Siegfeld later (*Milchwirt. Zentralbl.*, 1908, **351**) confirmed these results.

The "amyl alcohol" now used for the test is commercial amyl alcohol, obtained by fractionation from fusel oil, with b.pt. 128° to 132° C. It consists principally of a mixture of isoamyl alcohol (3-methyl-butanol; b.pt. 131·4° C.) and active amyl alcohol (2-methyl butanol; b.pt. 128° C., $[\alpha]^{20}_{D} = -5{\cdot}90°$), but the proportions of these vary with the source of the fusel oil, 14 to 22 per cent. of the active alcohol being present if the oil is produced by fermentation of maize or potato, and 48 to 58 per cent. in oil from molasses. The effect of this variation in composition of commercial amyl alcohol does not appear to have been considered in Siegfeld's work in 1903, and the nature of the constituents causing the occasional abnormal action of the reagent in the complicated reaction is not known. The results obtained by Houston (ANALYST, 1933, 151) on petroleum-free samples, and the general experience of other chemists during 30 years, indicate that neither of the two main constituents described above is the cause. Accidental contamination with petroleum is a subsidiary question, which can be dealt with by Droop Richmond's tests (*Dairy Chemistry*, 3rd Ed., p. 144) when it occurs.

It appears that the usual tests applied to amyl alcohol reagent for milk testing are not sufficient to ensure reliability for use in the Gerber test, and that they are, probably, a waste of time. The following requirements are suggested:

Commercial amyl alcohol.
Colourless to light yellow colour.

Sp.gr. at 15·5° C.	0·813 to 0·816
Boiling-point	124 to 132° C.

Ten ml. of reagent should mix with 10 ml. of hydrochloric acid (sp.gr. 1·16), and further addition of 1·0 ml. of water should cause permanent turbidity.

A sample of milk tested by the Gerber process with the specimen should give a result agreeing within 0·05 per cent. with the percentage of fat determined on the same milk by the Röse–Gottlieb test.

A. MORE

GOVERNMENT LABORATORY,
LONDON

A COLORIMETRIC METHOD OF DETERMINING OXALIC ACID

A colorimetric method of determining tartaric acid has been based by Underhill, Peterman and Krause (Analyst, 1932, **57**, 586) on the red coloration given by that acid with sodium metavanadate. Unfortunately, this method has the drawback that the intensity of the coloration is greatly reduced by the presence of material amounts of other organic acids, such as formic, citric, malic, succinic, or oxalic acid.

A more stable coloration is obtained by treating tartaric or oxalic acid with sodium metavanadate and hydrogen peroxide to form what appears to be a blood-red pervanadic complex. Mineral acids (which produce a pervanadic acid of similar colour) must not be present. The reaction with oxalic acid is approximately four times as sensitive as that with tartaric acid, but the difference is hardly sufficiently pronounced to be used as a means of distinguishing between the two acids. In dilute solutions the colour is reddish-orange.

In the absence of tartaric acid, which may be ensured by applying Fenton's colour reaction with ferrous sulphate, hydrogen peroxide and sodium hydroxide (*cf.* Analyst, 1933, 237), the reaction may be used for the colorimetric determination of small amounts of oxalic acid, in the presence of formic, acetic, citric, malic, or succinic acid.

The reagents required are a 1 per cent. solution of sodium metavanadate, and hydrogen peroxide (10 vol.). On treating 5 c.c. of a 0·1 per cent. solution of oxalic acid with 5 c.c. of the reagent and adding 3 c.c. of hydrogen peroxide, an orange-red coloration is produced, and the colour is not destroyed by increasing the amount of peroxide up to 10 c.c. The limit of sensitiveness of the reaction is about 3 parts of oxalic acid in 10,000.

Citric acid (5 c.c. of a 1 per cent. solution), treated with 5 c.c. of the reagent and 3 c.c. of hydrogen peroxide, gives a yellow tint, but, on then adding 3 c.c. of 0·1 per cent. oxalic acid solution, a distinct red coloration is produced.

Five c.c. of a saturated solution of citric acid, treated with 5 c.c. of the reagent, give an evanescent red colour, and, on then adding 3 c.c. of hydrogen peroxide, a yellow colour is produced.

When a small amount (0·1 c.c.) of hydrogen peroxide is added to a mixture of saturated citric acid solution and the vanadate solution, a red coloration results, but the colour is instantly discharged on increasing the amount of hydrogen peroxide to 1 c.c., and, on then adding 0·3 c.c. of 1 per cent. oxalic acid, the red-orange colour of the oxalic complex appears.

Succinic and malic acids in saturated solution also give only transient red colorations with sodium metavanadate and hydrogen peroxide. For quantitative work the coloration may be compared in Nessler glasses with that given by a solution of pure (A.R.) oxalic acid standardised on alkali. In a test experiment a commercial sample of oxalic acid gave results by titration agreeing well with those obtained by the colorimetric method.

As an example of the application of the method, the following experiment may be cited:—The juice from the leaf-stalk of a begonia plant was found to contain 0·83 per cent. of oxalic acid, calculated on the original material.

It would doubtless be possible to determine oxalic and tartaric acids together (in terms of oxalic acid) by this method, and then to determine the tartaric acid alone in the original solution by Anderson, Rouse and Letonoff's adaptation of Fenton's method (*loc. cit.*).

C. Ainsworth Mitchell

THE MINERAL CONSTITUENTS OF *ARTEMISIA AFRA*

A KNOWLEDGE of the mineral constituents of the leaves of *Artemisia afra* is of some interest, since, as the leaves yielded an essential oil, a preliminary investigation of which appeared in the *Perfumery and Essential Oil Record* of December, 1930, it may be of some value when the plant is to be cultivated for a more detailed study of the oil itself. An analysis of the dried leaves gave the following result:

K_2O, 3·32; Na_2O, 1·19; MgO, 0·68; CaO, 1·95; P_2O_5, 0·79; Fe_2O_3, 0·03; Cl, 0·57 per cent. Protein ($N \times 6{\cdot}25$), 17·63; total ash, 8·94; silica, 1·05 per cent.

G. W. B. VAN DER LINGEN

FUEL RESEARCH INSTITUTE,
LYNNWOOD ROAD, PRETORIA, S. AFRICA

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T. H. P.

Department of Scientific and Industrial Research

REPORT OF THE WATER POLLUTION RESEARCH BOARD FOR THE YEAR ENDED 30TH JUNE, 1932
WITH REPORT OF THE DIRECTOR OF WATER POLLUTION RESEARCH*

THE general depression in industry has not only caused reduction in the quantities of many trade effluents, but has also retarded progress of investigations into their treatment.

BEET SUGAR FACTORIES EFFLUENT.—Of the investigations in progress, that of the Beet Sugar Factories Effluent has included the inoculation of a percolation filter on a semi-commercial scale by certain organisms efficient in oxidising sugar. Results of the season's experiment showed that the inoculated filter gave a percentage filtration only very slightly better than that of the filter not previously inoculated. The bacteria used were able to maintain themselves in presence of other strains, and further investigations should lead to the selection of more efficient strains.

BIOLOGICAL FILTRATION OF MILK FACTORY EFFLUENTS.—Determination of the biochemical oxygen demand of effluents containing milk showed that a 1·3 per cent. solution of milk took up in 5 days about the same amount of oxygen as a 0·2 per cent. solution of sucrose, but that when solutions of this strength are supplied to the percolation filter the growth of film was much quicker and more copious than with sucrose. The liquid may be diluted, or a special device used, such as the wood-lath pile of Levine, in which the space between the laths may be adjusted so as to secure adequate aeration. Experiments are being made with a filter containing gravel, built in sections, with the top sections replaced by wood laths. The high alkalinity of the wash-water in milk factories (owing to use of soda) appears only to delay establishment of the film, and, provided the concentration of milk is adequate, the production of carbon dioxide quickly reduces the p_H values from 10 to 8, with formation of sodium bicarbonate, which does not seem to depress the bacterial oxidation.

SURVEY OF THE RIVER TEES.—*Chemical Poisoning of Fish.*—The completed hydrographical observations have been published as Water Pollution Technical Paper No. 2 (price 5s. 6d. net), and further measurements have now been made at different levels of the quantities of fresh water passing several points in stretches not subject to tidal influences. An investigation into the high mortality of salmon and sea trout smolts during the annual seaward migration showed that the dissolved-oxygen deficiency of the estuary waters was not by itself sufficient to account for it. The most important group of discharges into the estuary consisted of coke-oven or similar effluents, which were toxic owing to either tar acids or cyanides. More than 1000 kilos. of the former (calculated as phenols) and 400 kilos. (as cyanogen) of the latter are discharged daily. The tar acids were never found in sufficient concentrations to be toxic to fish, but the cyanides were frequently present in lethal concentrations, and, of 283 samples of water examined, 138 were found to be toxic. Confirmatory evidence was supplied by the fact that the gills of the poisoned fish were markedly brighter than normal.

Reduction of Cyanides in Effluents.—A remedy was found by mixing the cyanide-containing effluent intimately in the presence of lime with spent-pickle liquor, which consists mainly of a strong solution of ferrous chloride, and is

* **Obtainable at Adastral House, Kingsway, W.C.2. Price 1s. 0d. net.**

produced as a waste product in the cleaning of iron and steel. A large reduction of cyanide is also obtained by spraying the effluent as a fine mist at a temperature of about 60° C.

Toxicity of Tar Acids in Effluents.—On addition of a sub-lethal concentration of para-cresol to a solution of cyanide no increase in toxicity was observed, but concentrations of para-cresol and phenol, separately innocuous to trout, may, when present together, form a highly toxic solution, the two substances being interchangeable. The chemically-related substances para-cresol and xylenol, however, were found to be only partly interchangeable. In order to determine the effect of a toxic substance discharged into an already polluted stream it is therefore necessary to know if any interchangeable or semi-interchangeable substances are already present. Sewage has an accelerating action on the decomposition of phenolic substances under aerobic conditions, but apparently not on cyanides: Fresh sewage under aerobic conditions has no injurious effect on the fish population until depletion of oxygen has become marked, and may have affected the food supply.

The brown colour of the peaty Tees water, due to presence of peat colloids, may be removed by treatment with alumino-ferric with a ratio of Al : Fe of 4 : 1, provided that the p_H value of the water is suitably adjusted.

TREATMENT OF CORROSIVE AND PLUMBO-SOLVENT WATERS.—Preliminary experiments have been begun to study the rate of attack on lead by different waters; the influence of methods of cleaning specimens of lead on the subsequent action of waters on the metal, and the effects produced by electric power leakage to leaden water pipes.

ACTIVATED SLUDGE PROCESS OF SEWAGE TREATMENT.—The work during the year has been partly directed to a study of the factors involved in the absorption of oxygen, and also to devising a more satisfactory alternative method of following changes in oxygen-demand in the experimental tank.

Considerable work has also been done on Colloids in Sewage and on the treatment of Gas Works Effluent.

An investigation of the methylene blue test for measuring the stability of sewage and sewage effluents has led to modifications which enable this test to be carried out in a few hours or less instead of several days.

BASE EXCHANGE OF WATER SOFTENERS.—It has been found that when the single-stage process of regeneration is used, the base-exchange values of typical materials rise progressively as the time of contact with a 5 per cent. solution of salt is increased from 2 to 90 minutes. Further, the quantity of water which can be softened by a given amount of base material without further regeneration decreases rapidly as the concentration of salt in the hard water is raised from 0 to 1 per cent.

D. G. H.

THE INVESTIGATION OF ATMOSPHERIC POLLUTION

REPORT OF OBSERVATIONS IN THE YEAR ENDING 31ST MARCH, 1932*

THIS Report (the eighteenth of the series) is on the same lines as that for the previous year (ANALYST, 1932, **57**, 249). The report of the Standing Conference to the Co-operating Bodies draws attention to the necessity in large towns of a number of gauges in representative positions if comparisons are to be made.

* Published 16th March, 1933, pp. 102. Obtainable at Adastral House, Kingsway, W.C.2. Price 5s. 0d. net.

THE REPORT OF THE ATMOSPHERIC POLLUTION RESEARCH COMMITTEE

1. SULPHUR GASES IN AIR.—Regular daily observations have been instituted at 10 stations, by the method published last year, which gives actual concentration of sulphur gases, and the observations show that the highest recorded figures are for Barnsley in November (1·5 parts per million), and Salford, Regent Road, in February (1·63 p.p.m.). Foggy days showed a much higher concentration. An alternative method, involving analyses only once a month, has been evolved at the Building Research Station, and this is being tested at 8 stations where the standard method is used. The effective concentration or "activity" of atmospheric sulphur dioxide is measured by causing a prepared surface of lead peroxide to absorb the sulphur dioxide, and then determining the lead sulphate formed. The method is simple and the rate of absorption is independent of the humidity of the specimen, the subsidiary oxidation processes, and the insolubility of the product. The standard surface of lead peroxide is formed on a cotton fabric held by a porcelain cylinder of such dimensions that an area of 100 sq. cm. of the absorbent is exposed. The cylinder, which may be mounted on a table provided with a cowl, is held vertically by means of a fly-nut (2 B.A. thread) to a tapped bush fixed centrally in the table beneath the cowl. The fabric, after exposure for one month, is stripped off and treated with 5 grms. of A.R. anhydrous sodium carbonate in 60 ml. of water, and after standing with occasional stirring for at least 3 hours, is boiled in a glycerin-bath for half an hour, the volume being kept nearly constant, and is then filtered. The filtrate and washings are acidified with hydrochloric acid, and the sulphate is precipitated with barium chloride. In order to correlate results obtained by the two methods, it will be necessary, in the lead peroxide method, to take into account movement of air, since the method is a direct index of the activity of sulphur impurities.

2. OWENS' JET DUST COUNTER.—A new method of dust counting is being completed whereby a measured volume of air is passed through a narrow channel containing an electrically-heated filament, and the dust particles become deposited by thermal precipitation on plates on either side of the filament.

3. DEPOSIT GAUGE.—The investigation at Kew on the pollution gauge has been reported on (Appendix). It is concluded that such gauges, exposed side by side, should give practically the same rainfall, month by month, but discrepancies in the records of deposited impurity may be of the order of 30 per cent., although over the whole year the margin of doubt in the totals is not more than about 10 per cent. Both rainfall and impurity records are reduced by placing the gauge in the shelter of a house. The proportionate reduction is greater for rainfall, but the soluble and insoluble impurities are reduced in about the same ratio. It is necessary to take precautions with the gauges to avoid extraneous water entering, and protection of the receiving bottle from frost may be achieved by surrounding the gauge with a metal cylinder.

4. DEPOSITED IMPURITY.—The method suggested by Professor Cohen for obtaining an index of deposited impurity by exposing horizontal glass plates for stated periods, and then measuring them for tarry matter is not recommended, as it was found that the amount of tar deposited bore a widely varying ratio to the amount collected in the gauges.

5. PROTECTION OF DEPOSIT GAUGES.—The insertion of a rubber bag in the deposit-gauge receiving bottle as a guard against bursting by frost is not being taken up, as it was found to interfere with acidity observations.

RECORD OF OBSERVATIONS

During the year 95 deposit gauges and 13 automatic filters were in operation. The maximum and minimum monthly deposits as metric tons per sq. km. (conversion tables are given, and the figures are also tabulated in English units) were: *Tar:* Ashington (High Market), 73; Dewsbury, Whitley, 1; *other insoluble carbonaceous matter:* Burnley (Town Hall), 449; Leicester (Western Park), 39; *ash of insoluble matter:* Ashington (High Market), 1364; Leeds (Temple Newsam), 67; *ash of soluble matter:* London (Ravenscourt Park), 685; Wakefield (Clarence Park), 80; *total solids:* Ashington (High Market), 2415; Leicester (Western Park), 283; *rainfall:* Salford (Drinkwater Park), 94 mm.; London (Victoria Park), 39 mm.

More stations show a reduction of deposit than an increase, and, by the use of "general average" figures (the method of obtaining which is explained in detail), the greatest improvement appears to be in the deposit of tar which was 80 per cent. of the average, whilst total solids were 86 per cent. A marked increase of sulphur deposited at Ravenscourt Park, London, is again reported, the figure being 290 per cent. of the general average, but an explanation is not yet forthcoming. Golden Lane, London, also had an abnormally high deposit. The only stations showing a reduction in all the components of deposit were Glasgow (Richmond Park and Victoria Park); Leeds (Hunslet) and Marple; Newcastle-on-Tyne (Westgate Road); Rochdale (Electricity Works), and Wakefield (Clarence Park). A large number of stations return a definitely acid deposit, particularly the Midland manufacturing cities, whilst Birmingham (West Heath), Kingston-upon-Hull (Central and Suburban), amongst others, show consistently alkaline deposits.

D. G. H.

Connecticut Agricultural Experiment Station

THIRTY-SIXTH REPORT ON FOOD PRODUCTS, 1931

THE work summarised by Dr. E. M. Bailey in this Report was done in connection with the inspection and analysis of foods and drugs for purposes of control as provided by the statutes. Most of the samples examined were submitted by the Dairy and Food Commissioner.

GRADES OF EGGS.—The so-called "cold-storage egg law" provides that eggs that have been preserved by any artificial process, or that have been kept in storage for 15 days or more in any place where the temperature is reduced by artificial refrigeration, or that have been incubated for 24 hours or more, shall be marked "cold-storage eggs," "preserved eggs," or "incubator eggs," as the case may be, if such eggs are offered for sale. Wholesalers are required to state on invoices whether eggs sold are "fresh" or of the classifications noted above. This law has been in effect for many years, and is under the administration of the Dairy and Food Commissioner.

More recently a law authorising the Commissioner of Agriculture to establish grades for fresh eggs has been enacted (Public Acts, 1931, Sec. 336a). This Act prohibits the sale or the advertising of eggs as "fresh," "strictly fresh," "hennery," "new laid," or like descriptions if such eggs are not, in fact, fresh eggs. The Act specifies the characteristics of fresh eggs, to be determined by candling, as follows: Air cells not more than 0·25 inch deep, localised and regular; whites firm and clear; yolks allowed to be visible; no visible germ development.

Some confusion arose in the trade in attempting to abide by the requirements of both laws. To meet this difficulty the following ruling has been made, with the concurrence of the Commissioner of Agriculture and representatives of the trade.

Section 2453 of the General Statutes relates to the sale of eggs and prescribes how eggs of various classes therein named shall be labelled. The intent of the Statute is that eggs sold or offered for sale shall be labelled and invoiced in a manner that is informative of their character. It is recognised, however, that there are at times in the channels of trade, eggs that are not properly designated by the terms named in the statute, *i.e.* "cold storage eggs," "preserved eggs" or "incubated eggs," and that do not have the characteristics necessary to warrant designation as "fresh eggs."

For the guidance of the trade, and to relieve the uncertainty that has arisen as to an acceptable labelling for eggs of this type and class, it is held that an adequate designation for such eggs will be the unqualified name "eggs." The understanding of this term is that eggs so designated do not conform to the specifications laid down for "fresh eggs" (Chapter 124, Public Acts, 1931), and are not "cold storage," "preserved" or "incubated," but are, nevertheless, wholesome and edible eggs.

Experience has shown that eggs conforming to the specification given for fresh eggs will generally have an ammoniacal nitrogen content of less than 2 mgrms. per 100 grms. of egg. Cold-storage eggs may have considerably enlarged air spaces, but the ammoniacal nitrogen will be of about the same order as that of fresh eggs. If, however, eggs are dipped before being placed in cold storage, the air spaces and ammoniacal nitrogen may not be appreciably different from those in fresh eggs. Examination of the shell in such cases should indicate the fact of dipping. Eggs that have been dipped but not subsequently held at reduced temperatures, will show small air spaces, but the ammoniacal nitrogen will generally be greater than is found in fresh eggs. In stale eggs air spaces will be large and the ammoniacal nitrogen high.

With careful methods of handling, eggs can be shipped long distances and still qualify as fresh. Thus a lot of Californian eggs, not dipped and not refrigerated except during transit, were found to have air spaces less than 0·25 inch in depth, and to contain less than 2 mgrms. of ammoniacal nitrogen per 100 grms. of egg.

Of 101 samples examined during the year, 44 were improperly labelled.

COLOURING OF OLEOMARGARINE.—Federal laws regulating taxes upon oleomargarine impose a tax of ¼ cent per pound upon uncoloured oleo and 10 cents per pound upon coloured oleo. Formerly the product was held to be coloured if ingredients of such character and in such amounts were added as to serve the sole purpose of producing colour. Naturally coloured fats that served as *bona fide* and substantial part of the article did not bring the product within the classification of coloured oleomargarine. An act of Congress approved March 4, 1931, however, amended previous regulations in this respect, and at present coloured fats or oils may not be used in the manufacture of oleomargarine if they impart a shade of yellow greater than 1·6 degrees of yellow and red collectively, unless the product is classed as coloured and taxed accordingly. Since a tax of 10 cents per pound is prohibitive, oleomargarine will no longer be made from fats possessing any considerable degree of yellow.

Artificial colour may still be added to butter, and the amount is not restricted.

GLUTEN FLOUR.—The standard for gluten flour specifies that this product shall not contain more than 10 per cent. of moisture and, on a water-free basis, not less than 7·1 per cent. of nitrogen, not more than 56 per cent. of nitrogen-free extract, and not more than 44 per cent. of starch. The factor 5·7 is used in estimating protein.

Five samples, representing well-known brands of gluten flour, were examined, and all met the standard for moisture and nitrogen.

GLUTEN BREAD.—There is no official definition or standard for gluten bread, but since the article is used because of its reduced carbohydrate content as compared with ordinary white bread, the flour ingredient should be gluten flour.

Breads that do not differ essentially from white bread should not be designated as gluten breads.

The following are typical analyses of gluten breads examined during the year:

	Moisture Per Cent.	Ash Per Cent.	Protein ($N \times 5{\cdot}7$) Per Cent.	Fibre Per Cent.	Nitrogen-free extract Per Cent.	Fat Per Cent.
1	38·15	2·70	25·01	0·18	31·47	2·49
2	45·01	1·94	27·04	0·27	22·10	3·64
3	7·45	1·17	43·95	0·28	38·76	8·39
4	34·38	2·26	20·68	0·22	34·91	7·55
5	41·60	1·58	24·12	0·24	28·43	4·03
Typical common white bread	35·3	1·1	9·2	0·5	52·6	1·3

No. 3 was a so-called aerated bread, and was not a moist but an air-dry loaf.

MAYONNAISE.—The minimum percentage of egg yolk and oil (78 per cent.) specified in an earlier definition, has been deleted, and the only numerical standard now provided is a minimum of vegetable oil, namely, 50 per cent. At the same time it is still pertinent to know the proportion of egg or egg yolk in mayonnaise.

The present tentative method of estimating egg in egg products by determining the lipoid phosphoric acid, is admittedly only approximate. Apparently the egg content can be estimated with reasonable accuracy in this way in freshly made mayonnaise, but it has been found that laboratory-made dressings undergo some change when kept, which results in a transformation of lipoid phosphoric acid, and the same change has been noted in commercial products. The magnitude of this change is sufficient to render the estimates of egg yolk in mayonnaise that has been kept for 6 weeks or longer quite untrustworthy. The total phosphoric-content, however, remains practically constant, and is thus a safer basis for the evaluation of egg-content than is the lipoid phosphorus. The following results illustrate this point:

Lipoid P_2O_5 and total P_2O_5 in mayonnaise at intervals after manufacture

	Lipoid P_2O_5 Per Cent.	Total P_2O_5 Per Cent.
Laboratory sample A, initial ..	0·091	0·139
after 6 weeks ..	0·065	—
Commercial sample B, initial ..	0·063	0·102
after 3 months ..	0·043	0·099
after 6 months ..	0·036	0·100
Laboratory sample C, initial ..	0·174	0·277
after 2 months ..	0·166	0·274

In estimating egg-yolk-content from the total phosphoric acid value a factor must be chosen, and this must be based upon average values, as in the case of the factor for lipoid phosphoric acid. For the laboratory mayonnaise, yolks of fresh eggs were used, and the total phosphoric acid content of the yolks was about 1·4 per cent. Results reported by Cook (*Allen's Commercial Organic Analysis*, 4th Ed., Vol. **8**, p. 446) show 1·39 per cent. for boiled yolks of fresh eggs, and an average 1·4 per cent. for yolks from cold storage eggs. Unpublished results (furnished by courtesy of another investigator) show about 1·4 per cent for fresh and "commercial" fresh egg yolk, and a little lower (1·3 per cent.) for yolks from cold storage eggs. It seems fair to assume 1·4 per cent. as the average total phosphoric acid content of egg yolk, for purposes of calculation.

If cider or malt vinegar has been used in the dressing, some of the phosphoric acid will come from this source (0·01 to 0·02 per cent. in experimental dressings with cider vinegar), but such a correction factor cannot be applied to commercial products.

The following results were obtained in estimations of the egg yolk in experimental and commercial samples, in which the factor 0·89 was used for the calculation

from the lipoid phosphorus and no correction for non-egg phosphorus was applied to the total phosphoric acid:

Sample		Estimated egg yolk, from: Lipoid P_2O_5 Per Cent.	Total P_2O_5 Per Cent.	Formula Per Cent.
Commercial sample A, initial	..	7·1	7·3	7·0
after 3 months	..	4·8	7·1	—
after 6 months	..	4·0	7·1	—
Laboratory sample B, initial	..	19·6	19·8	18·8
after 2 months	..	18·7	19·6	—
Commercial sample C, initial	..	14·8	15·1	15·0
Commercial sample D, initial	..	8·4	10·0	—

The following table gives typical results obtained in the examination of various well-known commercial mayonnaises.

Brand	Total solids Per Cent.	Ash Per Cent.	Protein Per Cent.	Undetermined (by diff.) Per Cent.	Fat, total Per Cent.	Salt Per Cent.	Acidity Per Cent.	Total P_2O_5 Per Cent.	Egg yolk estimated from total P_2O_5 Per Cent.	Oil, estimated Per Cent.
Ames, Quality No. 1	85·96	1·34	1·88	2·04	80·70	1·02	0·40	0·125	8·9	77·7
Heinz	85·60	1·04	1·88	0·69	81·99	0·89	0·40	0·120	8·6	79·1
Kraft-Phoenix Cheese Co.	86·07	1·29	1·44	2·85	80·49	1·12	0·31	0·101	7·2	78·1
Swift & Co. ..	80·41	1·99	1·63	4·24	72·55	1·64	0·50	0·105	7·5	70·1
Seidner ..	76·17	1·69	2·75	2·66	69·07	1·14	0·75	0·212	15·1	64·1
Underwood & Sons	78·44	1·73	2·50	2·90	71·31	1·32	0·75	0·164	11·7	67·4

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Chemical Changes in the Fat of Frozen and Chilled Meat. Part V. The Effect of Smoking and the Influence of Atmospheric Humidity on the Keeping Properties of Bacon. C. H. Lea. (*J. Soc. Chem. Ind.*, 1933, **52**, 57–62T.)—Previous experiments have been extended to determine the effect of smoking on the keeping properties of freshly cured bacon at normal and cold-storage temperatures, and to find what influence humidity has on the deterioration of the fat. During smoking certain substances acting as anti-oxidants, appear to be absorbed from the smoke, so that exposed fat and that immediately beneath the rind resist oxidation considerably longer than similarly situated fat of green bacon. Eventually a zone of oxidation appears beyond the penetration limit of the smoke, and in the case of smoked bacon stored at $-10°$ C. for 3 months the maximum peroxide-oxygen content was reached at approximately $\frac{3}{4}$ inch from the exposed surface of the back fat. Bleaching of the blood-pigment of the fat does not appear to be correlated with oxidation. A relative humidity of 60 or 75 per cent. was satisfactory for storing bacon, and the fat developed no

appreciable taint in 32 days, and at humidities of 90 and 100 per cent., moulds, yeasts, and bacteria readily attacked it, but with the appearance of tainting due to these growths oxidation stopped, the two types of rancidity not developing at the same time in one sample of fat. Experiments undertaken to find whether the small peroxide-oxygen values always found for the superficial fat of freshly-cured bacon were due partly or wholly to traces of nitrite derived from the cure, did not furnish conclusive evidence, but the balance seems to be in favour of the values being due rather to oxidation. (*Cf.* ANALYST, 1931, **56**, 759.)

D. G. H.

Oil-Content of Nine Varieties of Soya Bean and the Characteristics of the Extracted Oils. G. S. Jamieson, W. F. Baughman and R. S. McKinney. (*J. Agric. Res.*, 1933, **46**, 57–58.)—The proportion of oil and its characteristics were determined for several varieties of soya bean used in a previous protein investigation (*J. Agric. Res.*, 1933, **46**, 51–55). The oils were extracted with ether, but the percentage was found with petroleum spirit as solvent, although with soya there is little difference in the two extracts. The varieties of bean used were Dunfield (*a*), Manchu (*b*), Haberlandt (*c*), Virginia (*d*), Chiquita (*e*), Mammoth Yellow (*f*), Peking (*g*), Illini (*h*), and A.K. (*i*).

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Sp.gr. at 25/25° C. ..	0·9216	0·9218	0·9196	0·9198	0·9245	0·9224	—	—	—
$n_D^{20°}$ ..	1·4748	1·4749	1·4745	1·4743	1·4763	1·4748	1·4763	1·4749	1·4756
Acid value ..	—	—	—	—	—	—	1·4	1·5	1·6
Saponification value..	191·2	191·6	191·6	191·5	191·1	191·7	190·0	189·9	190·9
Unsaponifiable matter, per cent. ..	0·73	0·88	0·80	1·08	0·85	0·85	1·10	0·86	0·89
Iodine number (Hanus)	131·4	131·0	131·6	127·8	140·7	129·4	141·4	131·3	132·6
Thiocyanogen-iodine value	84·1	82·2	82·2	81·4	87·0	83·4	—	—	—
Saturated acids, per cent. ..	12·6	11·9	12·5	12·5	11·7	11·7	—	—	—
Unsaturated acids, per cent. ..	80·4	80·9	80·2	80·1	81·0	80·8	—	—	—
Iodine value of unsaturated acids (calculated)	162·6	161·5	162·1	157·8	172·4	159·1	—	—	—

The differences in iodine and thiocyanogen values are due to variations in the proportions of oleic, linolic, and linolenic acids present. D. G. H.

Study of the Kjeldahl Method [for the Analysis of Flour]. Comparison of Selenium, Copper and Mercury Catalysts. R. A. Osborn and A. Krasnitz. (*J. Assoc. Off. Agr. Chem.*, 1933, **16**, 110–113.)—The comparative efficiency of selenium and other catalysts in the analysis of flour by the Kjeldahl method was studied. One-grm. samples of gluten and ordinary flour were digested under similar conditions of heating (calibrated 400-watt electric heaters) with mixtures of 25 c.c. of sulphuric acid and 11 grms. of anhydrous sodium sulphate alone and mixed with the following, separately or in various combinations: 0·7 grm. of

mercuric oxide, 0·1 grm. of precipitated selenium, 0·2 grm. of selenium oxychloride, 1·0 grm. of copper sulphate crystals. The results showed that there was little difference in the minimum digestion period (60 to 75 minutes for gluten flour, and 40 to 45 minutes for ordinary flour) required for correct results with selenium, selenium oxychloride or mercuric oxide used separately; with copper sulphate the time required was greater. With mixed mercury-selenium catalyst the digestion time was some 25 per cent. less than the above. In all cases the total time of digestion was approximately 50 per cent. greater than the time necessary for "clearing." It was concluded that selenium or its oxychloride as catalyst has a slight advantage over copper sulphate, but no advantage over mercury oxide. Selenium oxychloride is less suitable than precipitated elemental selenium because it is objectionable to handle and relatively expensive. A combination of selenium with mercury oxide is to be preferred to a single catalyst. S. G. C.

Detection and Determination of Antipyrine in Pyramidone. J. Eury. (*J. Pharm. Chim.*, 1933, **125**, 208–212.)—To determine the amount of antipyrine present, 0·25 grm. of the pyramidone, 0·4 grm. of pulverised mercuric oxide and 200 c.c. of water are boiled together for 5 minutes, and cooled, and the solution is made up to 250 c.c. and filtered. Twenty c.c. of the filtrate are treated with hydrogen sulphide, and, if there is no black precipitate, no antipyrine is present. If there is a precipitate, 20 per cent. potassium iodide solution is added to 200 c.c. of the test solution. If there is no precipitate the proportion of antipyrine is small, and a minimum of 10 c.c. of the potassium iodide solution is added, but in the event of a precipitate being found, the potassium iodide is added until the precipitate is dissolved. A little starch paste is then added, followed by 0·1 *N* iodine solution until a persistent blue tint is formed. One c.c. of 0·1 *N* iodine solution corresponds with 0·0125 grm. of antipyrine. D. G. H.

Identification of Atoxyl. M. Wagenaar. (*Pharm. Weekblad*, 1933, **70**, 233–239.)—Atoxyl (the sodium salt of *p*-amino-phenyl-arsenic acid) is administered in association with quinine salts, the toxicity of the arsenic being about one-fiftieth of that present in arsenic pentoxide. It is soluble in 6 parts of cold water, sparingly soluble in alcohol and insoluble in ether. Silver nitrate produces a voluminous precipitate of plate-shaped micro crystals which are soluble in ammonia, and are re-deposited on evaporation (sensitiveness 0·01 mgrm., 1 : 300). Cadmium sulphate precipitates small crystals in radiating groups (0·05 mgrm., 1 : 100), and magnesium sulphate deposits large rectangular plates (0·02 mgrm., 1 : 300). The amino group reacts with a solution of furfural in oleic acid to form a red furfuryl phenyl methane colour which may be used to detect 0·1 mgrm. of atoxyl; a drop of the solution to be tested should be first evaporated with hydrochloric acid or treated with acetone (*vide infra*). Similarly, vanillin or piperonal gives a yellow colour, and the lignin present in a splinter of wood moistened with concentrated hydrochloric acid develops an orange colour (*cf.* Van Zijp, ANALYST, 1922, **47**, 35). Micro-modifications of the reaction with mercuric chloride (Flückiger and Gutzeit) are described, a crystal of the recrystallised reagent held in the gases evolved during the ordinary Marsh–Berzelius test for arsenic being coloured yellow if

3 mgrms. or more of atoxyl are present. Alternatively, the atoxyl is precipitated from a drop of solution on a microscope slide with a drop of acetone, the water is removed from the resulting milky precipitate of dextro-rotatory and negatively doubly-refracting crystals by means of a strip of paper, and the reagent is applied to the residue after evaporation of the acetone. Photomicrographs of the crystals obtained in the principal tests are given. J. G.

Biochemical

Fate of Tartaric Acid in the Human Body. P. Finkle. (*J. Biol. Chem.*, 1933, **100**, 349–355.)—Until recently no accurate method existed for the quantitative determination of small amounts of tartaric acid in the urine. Underhill, Peterman and Krause (*J. Pharmacol. und Exp. Therap.*, 1931, **43**, 351) reported a colorimetric method based upon the reaction between metavanadates and tartaric acid in which a golden red colour results; this identical method was developed independently by the author, who has used it during the past three years, and reports upon its accuracy. Experiments described demonstrate that tartaric acid (sodium tartrate) is not burned in the human body. When injected intramuscularly it reappears almost quantitatively in the urine within 10 hours, the major portion being excreted within the first 4 hours. Apparently the human body can neither oxidise nor otherwise transform this acid. When taken by mouth only about 20 per cent. of ingested tartrate is eliminated in the urine. At no time in the course of investigations have any traces of tartrate taken by mouth been demonstrated in the faeces. Tartaric acid is destroyed by fungi and by certain bacteria; it is probable that the portion of tartaric acid given by mouth which fails to appear in the urine (80 per cent.) is destroyed in the intestinal tract by bacterial action; 20 per cent. or less is absorbed before it is subjected to the destructive action of the intestinal bacteria, and is excreted in the urine. This would explain why previous workers found the urine acid and not alkaline after subjects were fed with grape juice. The conclusion that tartaric acid (sodium tartrate) cannot be utilised in the human body and is excreted by the kidneys, is at variance with previous reports, probably owing to the fact that in the earlier experiments such large amounts were injected into small animals that severe injury to renal tubules resulted; also the methods then available for determination of small amounts of tartaric acid were not so accurate as the methods used by the author. With the doses employed in this investigation on human beings renal damage did not occur, and it was therefore possible to recover practically all of the injected tartrate in the urine, and to demonstrate that none of this fruit acid is utilised by human beings. P. H. P.

Some Analyses of Egg-Shell Keratin. H. O. Calvery. (*J. Biol. Chem.*, 1933, **100**, 183–186.)—Analyses are reported for ash, moisture, sulphur, nitrogen and some of the amino acids present in egg-shell keratin. Shells, obtained from eggs not more than one day old, were washed, and then suspended in 3 to 5 per cent. hydrochloric acid to remove soluble inorganic material, washed, and subsequently digested several days with pepsin in hydrochloric acid for removal of digestible proteins. The keratin was washed thoroughly with distilled water, followed by alcohol and ether, dried in a vacuum desiccator over sulphuric acid for 48 hours,

and was ready for analysis. The results represent the values obtained from a mixture of the shell membranes, with any material not removed by the above procedure. The results obtained by the author are given in a table, together with the mono-amino acids of egg shell keratin determined by Abderhalden and Ebstein (*Z. physiol. Chem.*, 1906, **48**, 530), the ash, moisture, nitrogen, and basic amino acids determined by Plimmer and Rosedale (*Biochem. J.*, 1925, **19**, 1015) by the nitrogen-distribution method, and the cystine obtained by isolation by Mörner (*Z. physiol. Chem.*, 1901, **34**, 207). Abderhalden and Ebstein used 25,000 eggs, and obtained 450 grms. of protein; the author used approximately 800 eggs, and obtained 80 grms. of protein. The percentage values now reported by Calvery for egg-shell keratin on the basis of ash- and moisture-free protein are:—Ash, 0·05; moisture, 8·60; nitrogen, 16·57; sulphur, 3·78; tyrosine, 2·54; proline, 3·83; glutamic acid, 10·11; aspartic acid, 3·38; tryptophane, 2·61; cystine, 12·67; arginine, 8·88; histidine, 0·86; and lysine, 3·66. It is of interest to note that the ratios of arginine, histidine and lysine to each other are quite close to the ratios of 12 : 1 : 4, which Block and Vickery (*J. Biol. Chem.*, 1931, **93**, 113) have postulated are the ratios of these amino-acids in a true keratin. P. H. P.

Clinical Detection of β-Hydroxybutyric Acid in Urine and other Fluids of the Organism. J. Khouri. (*J. Pharm. Chim.*, 1933, **17**, 161–165.)—The method described consists in boiling the acidified liquid until all ketonic compounds are expelled, treating the cooled solution with hydrogen peroxide to convert the β-hydroxybutyric acid into acetone, and testing for the latter with salicylaldehyde. Ten c.c. of the liquid are boiled in a test-tube with one or two drops of phosphoric acid until the volume is reduced by one-half, water being added to the cooled solution to bring its volume to the original value. A small portion is then tested with salicylaldehyde to ascertain if all the ketonic substances have been eliminated. If this is so, the liquid is shaken for about a minute with a few cgrms. of powdered sodium peroxide and then tested with salicylaldehyde, which gives a red coloration with acetone.

If the original urine is highly coloured or contains a small proportion of sugar (below 1 per cent.), it should be first defecated with one-tenth of its volume of lead acetate solution, the excess of lead being removed by treatment with anhydrous sodium sulphate. Urines rich in glucose must be freed from this either by means of ammoniacal basic lead acetate or by Van Slyke's method with copper sulphate and lime. In either case, the resulting solution should be concentrated, especially if small amounts of the acid are to be detected.

The salicylaldehyde solution should be freshly prepared, and at first very little sodium peroxide should be used, more being taken for a second test if the first gives indistinct results. With some urines, such as those of diabetic patients, the oxidation yields non-ketonic compounds which react with salicylaldehyde like ketones. In these cases, the resulting liquid should be distilled from the test-tube and the first few drops of the distillate tested.

The method is probably applicable to blood serum or other body liquid, after this has been freed from albumin by treatment with metaphosphoric acid or otherwise. T. H. P.

Bicolorimetric Method for the Determination of Methaemoglobin. B. B. Clark and R. B. Gibson. (*J. Biol. Chem.*, 1933, **100**, 205–208.)—All previous methods for the quantitative determination of methaemoglobin are based upon indirect determination by the difference between total haemoglobin and active haemoglobin. A simple accurate bicolorimetric method for the direct determination of methaemoglobin is now described. Blood samples are diluted 1:100. Two standards are prepared: one composed of carboxyhaemoglobin, and the other of methaemoglobin. To prepare the methaemoglobin standard the diluted blood is treated with freshly-prepared potassium ferricyanide solution, and allowed to stand until the colour changes from red to brown, when no haemoglobin or oxyhaemoglobin spectrum should be present. The solution is then saturated with carbon monoxide gas. For the carboxyhaemoglobin standard the blood is treated with an ammoniacal solution of sodium hydrosulphite and carbon monoxide. The unknown specimen is saturated with carbon monoxide. Comparison is made in a Hastings bicolorimeter. For comparison, methaemoglobin was determined by the difference between total haemoglobin (as determined from the iron content) and active haemoglobin (as determined by oxygen capacity), and the results agree well over a wide range of percentages. The presence of the methaemoglobin spectrum is uncertain when less than 25 per cent. of methaemoglobin is present. Colorimetric comparison is relatively easy, since good contrast is obtained between the bright red colour of carboxyhaemoglobin and the brown colour of methaemoglobin. A slight turbidity which might develop is remedied if all the solutions are centrifuged before comparisons are made; for this reason the solutions are prepared in 15-c.c. centrifuge tubes. P. H. P.

Unsaponifiable Lipids of Ox-Liver. I. Methods of Separation; Crystalline Fractions. F. C. Freytag and H. G. Smith. (*J. Biol. Chem.*, 1933, **100**, 309–317.)—The association of the fat-soluble vitamins with the unsaponifiable fraction of lipids has stimulated study of the large number of complex substances found in this portion of plant and animal fats. Detailed investigation of ox-liver unsaponifiable matter was further prompted by the possible relationship of these compounds to nutritional studies being conducted with ox-liver. It is shown, by means of their differential solubilities in various organic solvents that the solid and liquid constituents of the unsaponifiable lipids of ox-liver are separated more effectively than is possible by crystallisation from a single solvent such as alcohol. A diagram shows the method of fractionation. Sterols constituted 64 per cent. of the unsaponifiable lipids. The properties of the cholesterol and of three of its derivatives indicated that it is identical with cholesterol obtained from other sources. Small amounts of dihydrocholesterol and ergosterol were also found. Nitrogenous substances were isolated in small amounts from the later fractions. Of these, lignoceryl sphingosine was identified. These substances are held to be partial cleavage-products of sphingomyelin and similar compounds rather than normal tissue constituents. The liquid fractions from ox-liver unsaponifiable matter probably include higher alcohols, hydrocarbons, vitamins, and as yet unidentified substances. P. H. P.

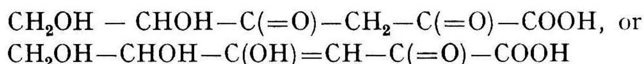
Unsaponifiable Lipids of Ox-Liver. II. Vitamins *A* and *E*; Anti-oxygens. F. C. Freytag and H. G. Smith. (*J. Biol. Chem.*, 1933, **100**, 319–322.)—The liquid residues of ox-liver unsaponifiable lipids have been examined for their content of vitamins *A* and *E* and anti-oxygenic material. The three fractions (referred to as Fractions II*b*, VI and VII*b*) were dark red, fluorescent, viscous oils. On the basis of colour tests, Fraction VI obtained from petroleum spirit, was practically sterol-free, whilst Fractions II*b* and VII*b*, from methyl alcohol, still contained sterols and also vitamin *A* in high concentration. By means of the preferential solubility of vitamin *A* in methyl alcohol, concentrates were obtained whose vitamin *A* value, judged by the intensity of ultra-violet light absorption at $328 m\mu$, was 100 to 125 times that of a commercial assayed cod-liver oil. By the same measure, applied to a concentrate of ox-liver lipids after minimum exposure to heat and oxygen, ox-liver fat may contain 3 to 5 times as much vitamin *A* as cod-liver oil. By vacuum distillation, vitamin *A* was concentrated in the fractions of lower b.pt., but with destruction of as much as four-fifths of the active material. Traces of anti-oxygenic material were present in all three fractions, but fractional vacuum distillation did not effect a concentration, as is the case with vegetable lipid concentrates. Vitamin *E* was present in relatively minute quantities in Fraction VI, the fraction comparable with that in which vitamin *E* is obtained from vegetable sources. (A single dose of 250 mgrms. of distillate of Fraction VI, administered to a rat deprived of vitamin *E* under the standard conditions for assay, provided sufficient vitamin *E* for normal gestation; similar fractions from wheat germ and lettuce are effective in doses of 10 mgrms. or less.) P. H. P.

New Colour Reaction for Hydroxyproline and its Use in Distinguishing the Scleroproteins. W. Morse. (*J. Biol. Chem.*, 1933, **100**, 373–377.)—A new colour test for hydroxyproline is given. Owing to the high content of this amino acid in collagen (14·1 per cent. in gelatin) as compared with that in other proteins (casein 0·23, zein 0·0, lactalbumin 0·0, edestin 2·0, keratin 0·0), especially the scleroproteins associated with collagen, the method serves at the same time as a test for collagen. The reagents required are:—(1) A secondary alcohol, such as methylhexylcarbinol (secondary octanol), (2) sodium peroxide, and (3) 5 *N* hydrochloric acid. Three drops of the alcohol and such an amount of the substance to be tested as will furnish approximately 1·0 mgrm. of hydroxyproline are covered with a few drops of distilled water, and about 0·5 grm. of sodium peroxide is then added. The contents of the tube are well mixed, and heated, gently at first, and then more strongly until nearly dry. The tube is thoroughly cooled under running water, the preparation still remaining colourless. While cooling is continued 2 c.c. of 5 *N* hydrochloric acid are poured into the tube, which is then left in a boiling water-bath to develop the characteristic amber-rose colour. Heating a secondary alcohol of the kind mentioned with strong alkali, accompanied by oxidation, is necessary in making the test. As a test for collagen, it must be noted that deamination of corium by means of nitrous acid inhibits the reaction; likewise, treatment of corium with formaldehyde, thus methylenating it, results in a colourless reaction. Hydroxyproline has been found to be bound loosely to

collagen. When the substance is finely minced, as in a Wiley mill with 0·5 mm. apertures, hydroxyproline actually may be washed from the substance to some extent. Trypsin-treated corium also gives up hydroxyproline to the liquor bathing it. Finished leather gives a positive reaction. The reaction is not in the nature of an indicator; if the rose colour is changed by neutralisation, re-acidification will not cause it to return; once obtained it will remain stable if boiled for an indefinite period. P. H. P.

Reduction-Capacity of Plant Foodstuffs and its Relation to Vitamin *C*. J. Tillmans, P. Hirsch and R. Vaubel. (*Z. Unters. Lebensm.*, 1933, **65**, 145–168.)—The method of titration with 2:6-dichlorophenol indophenol (*cf.* J. Tillmans and others, ANALYST, 1932, **57**, 260, 396, 397; S. S. Zilva, *id.*, 1931, **56**, 265; and O. Rygh and others, *id.*, 1932, **57**, 187, 188) has been modified, 10 c.c. of the solution of the dyestuff being standardised by titration, in the presence of 5 c.c. of a saturated solution of sodium oxalate, with a 0·01 *N* solution of ferrous ammonium sulphate containing 0·02 *N* sulphuric acid until no colour remains. The iron solution is itself standardised against potassium permanganate solution, and is stable for 3 months if stored in the dark and under nitrogen. The titration should occupy 30 to 45 seconds, and should be carried out in the shade. Determinations of the apparent equivalent weight, the solids and the ash were used to control the removal and purification of the reducing substance in potatoes and wild rose hips (*Rosa canina*). In the former case the best results were obtained after extraction for 2·5 hours with a mixture of 60 per cent. of acetone and 40 per cent. of 0·05 *N* sulphuric acid. In the latter, experiments are described involving adsorption, distillation in a vacuum, fermentation with yeast, precipitation with organic or inorganic substances, diffusion and dialysis. The procedure finally adopted may be summarised as follows, all operations being carried out in an atmosphere of nitrogen, and all distillations in a vacuum:—The extract obtained from the crushed, sound ripe fruit after digestion with 3 times its weight of 0·01 *N* phosphoric acid for 1 hour in carbon dioxide, and standing for 3 days, is evaporated until the solution contains 30 per cent. of total solids, and is then treated with 4 to 5 times its volume of pure acetone and allowed to stand overnight. The acetone solution is separated from the precipitate, again concentrated, treated with an equal volume of 10 per cent. lead acetate solution, and separated from the resulting precipitate. The solution and washings are freed from lead by means of hydrogen sulphide, united with the previous solution, and evaporated on sand (previously washed in acid and then water). The residue is extracted with pure methyl alcohol, and the new extract (concentrated to contain 15 per cent. of total solids) is precipitated with a 5-fold volume of pure ether. The treatment with lead acetate and acetone is repeated, and a yellow oil is then precipitated from the final extract by a mixture of methyl alcohol, ether, and an excess of petroleum spirit. This crystallises if kept overnight in the ice-chest, when it may be washed at —5° C. with acetone, and then with ether, recrystallised from methyl alcohol, and dried over calcium chloride in nitrogen at a low pressure. The yield was about 0·015 per cent., and determinations of the equivalent weight (iodimetrically, acidimetrically, and as described above), molecular weight (Barger and Rast, *Ber.*, 1921, **54**, 1979), m.pt. (184° to

189° C.), $[\alpha]_D^{21°}$ (+20·7° ± 0·7°), and chemical reactions (positive Molisch reaction and red colour with ammonia), indicate that the substance is identical with Szent-Györgyi's ascorbic acid (*Biochem. J.*, 1928, **22**, 1387; *Nature*, 1932, **129**, 690). Evidence in favour of the structures



$$CH_2OH - CHOH-C(=O)-CH_2-C(=O)-COOH, \text{ or}$$
$$CH_2OH-CHOH-C(OH)=CH-C(=O)-COOH$$

is discussed, and experiments on guinea-pigs are described which show that 0·5 mgrm. per day per animal is sufficient to prevent scurvy. W. Kollath contributes an account of the histological observations on which this conclusion is based.

J. G.

Toxicological and Forensic

Arsenic, Lead, and Chromium in Kindergarten Materials. E. Merres and R. Turnau. (*Z. Unters. Lebensm.*, 1933, **65**, 182–185.)—The following are typical figures for the percentages of arsenic, lead and chromium, respectively, in certain kindergarten materials:—*Wax crayons.*—Light yellow, 0, 7·2, 2·5; light green, 0, 5·2, 3·3; olive green, 0·015, 0, 0; burnt sienna, 0·014, 0, 0. *Water colours.*—Burnt sienna, 0·300, 0, 0; chrome oxide green, 0, 0, 22·0. *Artist's colours in sticks.*—French green, 41·9, 0, 0 (18·7 per cent. of copper); chrome yellow, 0, 44·6, 8·4; saturn red (minium), 0, 62·5, 0. *Artist's colours in tubes.*—Kremnitz white, 0, 57·1, 0; cinnabar green, 0, 28·7, 3·2. *Pastels.*—Lemon yellow, 0, 0, 1·5 (10·3 per cent. of zinc); sea green, 0, 0, 6·3 (5·2 per cent. of zinc). No poisonous metals were found in quantities likely to prove dangerous in 19 samples of moulding materials, but they were found in 4 of 38 wax crayons, 2 of 36 samples of water-colours, and 1 of 14 coloured papers (0·45 mgrm. of arsenic in 100 square cm. of pale green paper). J. G.

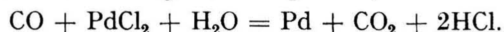
Removal of Lead and Tin from Tinned-Lead Tubes by Tooth-pastes. V. Froboese. (*Z. Unters. Lebensm.*, 1933, **65**, 176–181.)—Neutral or weakly-alkaline tooth-pastes from tinned-lead tubes were found to contain from 1 to 37 mgrms. of tin and 0·3 to 1·8 mgrm. of lead per 100 grms. of paste when purchased, the higher figures being obtained from tubes which showed signs of attack. These figures became 14 to 140 and 0·8 to 3, respectively, after storage for about 4 weeks, although storage for longer periods (8 weeks to 2 years) produced very little further increases, and in some cases decreases. Paste from a lead-free tin tube contained 2·7 mgrms. of tin (lead absent) on the day of purchase (*i.e.* less than most of the tinned-lead tubes), and that from a tin tube containing 0·35 per cent. of lead contained 42 mgrms. of tin and 0·28 mgrm. of lead per 100 grms. of paste after storage for 4 weeks. The electrical conductivities of the pastes were measured in a cylindrical glass tube (9 × 16 mm.) closed at each end with a platinum plate, but no definite relationship to the lead- or tin-content seems to exist. The German regulations specify that for foods and drugs such packings should not contain more than 1 part of lead per 100 by weight, and that for cosmetics the tube should be tin-plated with tin which does not contain more than this amount of lead. J. G.

Microchemical Colour Reaction of *m*-Dinitrobenzene for the Forensic Detection of Benzene. J. Peltzer. (*Chem.-Ztg.*, 1933, **57**, 162–163.)—To detect benzene in animal organs, these are acidified with dilute sulphuric acid, and the benzene is distilled off in steam and collected in carbon tetrachloride immersed in a cooling mixture. When the solution is shaken with a nitrating acid mixture, the benzene is converted into *m*-dinitrobenzene. As little as 0·001 mgrm. of the nitro-compound may be detected by treating it with 30 per cent. sodium hydroxide solution and shaking with an equal volume of acetone, which assumes a violet colour. This colour is still apparent if 0·0005 mgrm. of *m*-dinitrobenzene is dissolved, in a test-tube (1 cm. in diameter), in 0·05 c.c. of alcohol, and the solution is treated with 10 drops of the alkali solution and the whole is shaken with 0·2 c.c. of acetone. The reaction may be employed quantitatively. If the violet coloration of the acetone is somewhat intense, alcohol may be added until no further separation into layers occurs; a blood-red coloration appears, and this may also be used for the determination of *m*-dinitrobenzene. T. H. P.

Study of the Toxicity of Rotenone Hydrochloride, Acetylrotenone, and Rotenolone, using the Goldfish as Test Animal. W. A. Gersdorff. (*J. Amer. Chem. Soc.*, 1933, **55**, 1147–1152.)—For solutions of these three compounds two sets of curves have been constructed:—(1) Survival time curves, in which the time of survival in minutes is plotted against the concentration in mgrms. per litre, and (2) Velocity of fatality curves, in which 100/(time of survival) is plotted against the concentration. From these curves values are derived for the theoretical threshold of toxicity, that is, the concentration below which the substance does not cause death, and for the rate of increase of the theoretical velocity of fatality with increase in concentration; this rate is taken as the volume of water which must be added to one of the more dilute solutions containing 1 mgrm. of the toxic substance, to increase the survival time by one minute.

Solutions of rotenone hydrochloride and acetylrotenone become toxic to goldfish at very low concentrations (less than 0·002 mgrm. per litre), but with solutions of rotenolone the theoretical threshold of toxicity is 0·02 mgrm. per litre. T. H. P.

Detection of Small Amounts of Carbon Monoxide in Air. W. Ackermann. (*Chem.-Ztg.*, 1933, **57**, 154–155.)—Two methods have been compared:—(1) The gas was passed through a dilute solution of blood, fresh ammonium sulphide solution was added, and the mixture was examined in the spectroscope. (2) The gas was passed through a solution of palladium chloride, when separation of palladium occurred according to the equation,



$$CO + PdCl_2 + H_2O = Pd + CO_2 + 2HCl.$$

In the former case the smallest proportion of carbon monoxide detectable with certainty in admixture with air was found to be 0·13 per cent. (by volume), and 1 litre of mixture was required. Both lines of the absorption spectrum were plainly visible for 1 litre of mixture containing 0·2 to 0·4 per cent., but 5 litres were required if only 0·075 per cent. was present. In the second case, separation of palladium was visible after 3 minutes for 0·1 per cent. of carbon monoxide in 50 c.c. of mixture; 10 minutes for 0·05 (in 150 c.c.), and 20 minutes for 0·03 per cent.

(in 300 c.c.). The limit for convenient working is 0·015 per cent. in 1 litre of mixture, which is visible with certainty after 1 hour, but as an extreme case, 0·008 per cent. (in 6 litres) gives a visible deposit after 6 hours. For small quantities the solution should be filtered to render the palladium more easily visible, or it may be compared with a control consisting of untreated reagent. J. G.

Production of Carbon Monoxide from Paint in Sealed Compartments. S. F. Dudley, F. G. Edmed and R. C. Frederick. (*J. Ind. Hygiene*, 1933, **15**, 1–7.)—Previous work on iron oxide paints (*cf. id.*, 1931, **13**, 333, and F. H. Newington, ANALYST, 1931, **56**, 757) has now been extended to other materials used to paint sealed compartments in ships, namely, red lead, aluminium, bituminous and grease paints. These were exposed on metal by spreading on the inside surfaces of clean petrol cans, which were then sealed, and the gaseous contents examined by Newington's method (*loc. cit.*) after 1, 2 and 3 months at ordinary temperatures. Previous results were confirmed, namely, that as a rule, after 1 month, the concentration of carbon monoxide reaches a dangerous concentration. The following results were thus obtained:

	Carbon monoxide Per Cent.	Carbon dioxide Per Cent.	Oxygen Per Cent.
Iron oxide paint, after 1 month ..	0·355	1·78	12·11
,, ,, ,, ,, 3 months ..	0·39	3·20	3·40
Red lead paint, after 1 month ..	0·22	0·82	7·24
,, ,, ,, ,, 3 months ..	0·269	1·10	5·03
Aluminium paint, after 1 month ..	0·166	1·53	9·11
,, ,, ,, 3 months ..	0·189	1·20	7·31
Bitumastic solution, after 1 month	0·004	0·10	20·33
,, ,, ,, 3 months	0·004	0·13	20·21
Grease paint, after 1 month ..	0·006	0·10	20·54
,, ,, ,, 3 months ..	0·006	0·05	19·93

The changes shown in the table are attributed to the presence of linseed oil, and do not occur to any appreciable extent with bituminous and grease paints which do not contain this oil. Biological experiments with mice, in which the Hartridge reversion spectroscope (*cf.* Frederick, *id.*, 1931, **56**, 561) was used to determine the carbon monoxide in the blood, confirmed these results; it was also found, however, that the blood of a normal (*i.e.* unexposed) mouse sometimes contains a trace of this gas. Absorption of oxygen occurs more slowly than evolution of carbon monoxide, so that there is probably a critical stage at which sufficient oxygen may be present to support respiration in the presence of a lethal concentration of carbon monoxide. The gas-content will therefore depend on the area of the painted surface exposed, and on the period for which the compartment is sealed, although in the case of ships' holds the conditions are usually such as to exhaust practically all the oxygen. J. G.

Organic Analysis

Capric Acid from the Seed Fat of the California Bay Tree. C. R. Noller, I. J. Millner and J. J. Gordon. (*J. Amer. Chem. Soc.*, 1933, 55, 1227–1228.)—Extraction of the shelled and ground seeds with carbon tetrachloride yielded 58·5 per cent. of a fat, having m.pt. 28 to 30° C., saponification value 275·1, iodine value 5·7, and acid value 2·8, containing 2·1 per cent. of unsaponifiable matter, and showing no optical rotation in chloroform solution. Fractionation of the methyl esters of the free fatty acids showed that these acids approximately contain: caprylic acid 1, capric acid 37, and lauric acid 62 per cent. T. H. P.

Detection of Oxalic Acid as Oxalatomanganate. G. Lochmann. (*Chem.-Ztg.*, 1933, **57**, 214–215.)—The detection of oxalic acid and of manganese based on the red colour of the trioxalato-manganate ion, has been the subject of numerous investigations (*cf.*, *e.g.* Meyer and Nehrlich, *Z. anorg. Chem.*, 1921, **116**, 135), which are critically discussed in this paper; a modified method is now proposed in which the p_H value of the test solution, which has been found to have an important influence on the development of the colour, is controlled. A manganese oxide reagent is used, which is prepared as follows:—To a solution of 3 grms. of manganous chloride crystals and 3 grms. of ammonium chloride in 30 c.c. of water, 15 c.c. of 10 per cent. ammonia are added, followed by 30 c.c. of 2 per cent. hydrogen peroxide solution, in small portions at a time, with vigorous shaking; the precipitate is filtered off and washed with hot water until free from soluble chloride, dried, and powdered. *Method.*—To the liquid to be tested, sodium acetate is added, followed by either ammonia or dilute sulphuric acid until a drop of the solution, withdrawn on a glass rod, colours methyl orange paper brownish. To a portion of this solution a small quantity of the prepared manganese oxide is added, and the whole is well shaken for a short time. The development of a red colour indicates the presence of oxalic acid. The test should not be carried out in direct sunlight, as the red colour is readily bleached by it; in diffused daylight the colour lasts for about an hour. The sensitiveness of the method depends to some extent on other substances which may be present, but is normally about 1 part of oxalic acid in 2500 parts of solution. The sensitiveness is increased in the presence of limited amounts of phosphoric and hydrofluoric acids, but is diminished in the presence of aluminium salts and tungstates. Tartaric and malic acids interfere when present in relatively large amounts, owing to a dark brown colour being produced; this interference may be overcome either by first precipitating the oxalic acid as calcium oxalate or by boiling the solution, before the adjustment of the p_H value, with an excess of boric acid. Chloride, sulphate, nitrate, butyric, valeric, benzoic, and formic acids do not interfere. S. G. C.

Determination of Mineral Oil Retained by Leaf Surfaces after Spraying. L. H. Dawsey and A. J. Haas. (*J. Agric. Res.*, 1933, **46**, 41–49.)—Paraffin mineral oil retained by camphor leaves after spraying may be measured by the following method:—One hundred discs of 30 mm. diam. are cut from leaves picked at random, to make a single sample. This is introduced into a 200-c.c. Erlenmeyer flask and washed by rotation, first for 1 minute with 50 c.c., and then twice with

25-c.c. portions of ether to remove the last traces of oil. The ether is evaporated and the residue dissolved in a mixture of ether and absolute alcohol (1 : 1). The clear solution is cooled to —30° C. for 15 minutes or until waxy flakes are deposited. The precipitated wax and any undissolved dirt are filtered off under suction, the funnel being surrounded with a 22 per cent. sodium chloride constant-temperature mixture maintained at about —20° C. by means of small pieces of solid carbon dioxide. The wax is washed three times with 10 c.c.-portions of the mixture of alcohol and ether (previously chilled to —30° C.), and the filtrate and washings are evaporated to 10 c.c. and transferred to a calibrated Babcock skim-milk bottle, the flask being rinsed out three times with 5 c.c.-portions of ether. By immersing the bottle in hot water and holding the finger over the mouth the ether is evaporated through the capillary tube, and to the oily residue 6 c.c. of concentrated nitric acid (sp.gr. 1·42) are added. The mixture of acid, oil, and partly destroyed organic matter is heated to boiling, and, after the oily layer is clear, concentrated nitric acid is added to fill the neck of the bottle, and the whole is centrifuged. The length of the column of oil is measured to the nearest 0·1 mm.; the error in 5 experiments was under 1·6 per cent. By introducing certain variations the method was found applicable to pecan leaves (error less than 1 per cent.), and to satsuma leaves (error less than 2·5 per cent.). The natural wax extracted from equal areas of camphor leaves, in the presence of mineral oil, by ether and by chloroform, is shown to vary in different samples (*e.g.* for 10 samples extracted with chloroform, from 0·0331 to 0·0413 grm. per 100 discs of 30 mm. diam.). In a test experiment in which 0·1443 grm. of oil was added, the residue weighed 0·1753 grm., giving 0·0310 grm. for the extracted wax. D. G. H.

Determination by means of Nessler's Reagent of Methylols derived from Amides and Urea. J. Bougault and J. Laboucq. (*J. Pharm. Chim.*, 1933, **125**, 193–196.)—To between 0·1 and 0·5 grm. of the methylol a few c.c. of water and 35 c.c. of Nessler solution A and 20 c.c. of Nessler solution B (Gros formula) are added, and the mixture heated in a boiling water-bath. On cooling, 40 c.c. of 50 per cent. hydrochloric acid and 20 c.c. of 0·1 *N* iodine solution are added, the mixture is shaken to aid solution of the mercury salt, and the excess of iodine is titrated with 0·1 *N* sodium thiosulphate solution. With methylol derivatives (methylene dibenzamide and methylene methylol di-*o*-tolylurea) a preliminary acid hydrolysis, by means of 15 c.c. of 25 per cent. sulphuric acid, is carried on in a Kjeldahl distillation apparatus. Experimental results agreed closely with the calculated amounts. D. G. H.

Presence of Pyrethrolon and Methylpyrethrolon in Pyrethrum Flowers. C. B. Gnadinger and C. S. Corl. (*J. Amer. Chem. Soc.*, 1933, **55**, 1218–1223.)—All methods of evaluating pyrethrum either chemically or physiologically were condemned by Ripert (*Ann. Falsif.*, 1931, **24**, 325), who stated that the flowers contain from 0·1 to 0·4 per cent. of the methyl ether of pyrethrolon, which is determined as pyrethrins by the copper reduction method without possessing any toxicity to insects. A method is now described for separating pyrethrolon and its methyl ether from pyrethrins I and II. In petroleum spirit solution, the pyrethrins are not readily oxidised by 2 per cent. potassium permanganate solution,

the average loss under this treatment being only about 4 per cent. On the other hand, both pyrethrolon and its methyl ether are instantly oxidised under such conditions and are removed from the petroleum spirit solution. Freshly harvested pyrethrum flowers suffer about the same loss of pyrethrins by the permanganate treatment as solutions of the pure pyrethrins, but both flowers ten months old and pyrethrins which have undergone alteration by exposure to air show somewhat greater losses. Examination of pyrethrum flowers from America, Dalmatia, and Japan fails to indicate the presence therein of either pyrethrolon or its methyl ether in appreciable proportions. T. H. P.

Determination of Artificial Silk in Mixtures of Artificial Silk and Cotton Waste. P. McGregor and C. F. M. Fryd. (*J. Text. Inst.*, 1933, **24**, 103T.)—One grm. of the sample, freed from oil, and conditioned for 24 hours in an atmosphere of 60–65 per cent. relative humidity, is placed in a 300-ml. conical flask with 70 ml. of acidified calcium thiocyanate solution. This solution is prepared from the commercial solution of calcium thiocyanate usually containing about 80 grms. of calcium thiocyanate in 100 ml., adjusted by addition of water or of anhydrous calcium chloride until its boiling-point is 122–123° C., and by addition of glacial acetic acid to an acidity of about p_H 2·0. The process is dependent on close adherence to the prescribed strength and acidity of the reagent. The flask is heated on a water-bath at 70–80° C., and the contents are stirred mechanically at 400 revs. per minute for 30 minutes. The cotton residue, after being filtered off by suction on a Jena glass filter crucible, is re-heated as before with 30 ml. of the calcium thiocyanate solution for 10 minutes and again filtered. The wad is removed, boiled in two successive portions of water for 30 minutes, washed, dried in the oven, conditioned as before, and weighed. The result is calculated as a percentage on the original weight. R. F. I.

Determination of Water in Wool by Distillation. C. O. M. Steward. (*J. Text. Inst.*, 1933, **24**, 98T.)—A modification of the method of Dean and Stark is described, the drawbacks of which are overcome as follows:—A non-inflammable solvent is used, means are adopted for overcoming the tendency for drops of water to cling to the walls of the condenser tube, and the distillate is collected at a standard temperature so that the volume may be read off at once. Thirty grms. of a finished top are weighed on an automatic balance sensitive to 0·025 grm., and transferred to a 2-litre brass conical flask with 300 c.c. of dry perchlorethylene (sp.gr. 1·624; b.pt., 119° C.). A special distillation-tube is attached to the flask, the cork being painted with collodion flexile. The upper part of the descending arm of this tube is jacketed with a cold-water circulator, the lower part being graduated and ending with a glass tap like a burette. Distillation is carried out by means of a hot plate, the temperature of which is so adjusted that distillation is complete in 30 minutes. The distillation-tube should be cleaned after each estimation with alcohol and ether and periodically with chromic acid. The high density of the solvent eliminates the risk of charring the wool which floats on the surface. This method gives a slightly higher result than is obtained by heating half-a-pound of the sample in a conditioning-oven. R. F. I.

Inorganic Analysis

Sensitive Test for Gold. H. Holzer and W. Reif. (*Z. anal. Chem.*, 1933, **92**, 12–15.)—To 5 or 10 c.c. of the neutral or faintly acid solution to be tested are added 5 c.c. of a filtered 0·1 per cent. solution of α-naphthylamine hydrochloride and 2 to 3 c.c. of ethyl acetate. The test tube is vigorously shaken; after settling, the ester layer is coloured violet-red to faintly pink, according to the quantity of gold present. The test detects 0·008 mgrm. of gold at a dilution of 1 : 1,000,000. For minute amounts a parallel blank test is advisable. Substantial amounts of acid prevent the reaction; ferric and palladous salts give coloured solutions.

W. R. S.

Identification of Thallium as Thiocarbonate. M. Picon. (*Ann. Chim. Anal.*, 1933, **15**, 56–61.) (See *Compt. rend.*, 1932, **195**, 1274; ANALYST, 1933, 111.)

Determination of Tungsten with *o*-Hydroxyquinoline. S. Halberstadt. (*Z. anal. Chem.*, 1933, **92**, 86-89.)—The dilute, alkaline or neutral solution is treated with excess of a 4 per cent. alcoholic solution of the reagent, and, after heating to near the boiling-point, with dilute acetic acid to slight acid reaction. Mineral acid solutions are treated with ammonium acetate. The solution is boiled, the precipitate collected in a porous glass crucible and washed with hot water until the washings are colourless. It is dried at 120° C. and weighed. In accordance with the formula $WO_2(C_9H_6ON)_2$, the tungsten factor is 0·3650.

W. R. S.

Determination of Potassium by Titration of the Cobaltinitrite with Permanganate. P. L. Hibbard and P. R. Stout. (*J. Assoc. Off. Agr. Chem.*, 1933, **16**, 137–140.)—The method is similar to that described by Kramer and Tisdall (*J. Biol. Chem.*, 1921, **46**, 339), but possesses some advantage over it, as it can be more easily adapted to varying quantities of potassium by a modification of the titration process. It is claimed to be applicable to the rapid determination of quantities of 0·1 to 5·0 mgrms. of potassium when present in almost any material and to be particularly suitable for soil extracts, plant materials and biological solutions. Details of the method are not abstracted, since it is stated not to be suitable for occasional determinations, as it requires some experience in working it, and special equipment for filtering and washing the ppt., etc.

S. G. C.

Separation of Potassium and Sodium Chlorides by means of Aniline Bitartrate. J. Kunz. (*Helv. Chim. Acta.*, 1933, **16**, 259–261.)—*Qualitative.*—For testing for the presence of potassium chloride in sodium chloride, the dry material is dissolved in water to form a concentrated solution, and 9 volumes of 48 per cent. alcohol (1 vol. of 95 per cent. alcohol to 1 vol. of water) and 4 volumes of a 0·1 *N* aqueous-alcoholic solution of aniline bitartrate (prepared by dissolving 9·3 grms. of aniline and 15 grms. of tartaric acid in 1000 c.c. of the 48 per cent. alcohol) are added. The presence of potassium is shown by the precipitation of potassium bitartrate, which may be filtered off after 15 minutes and washed with 48 per cent. alcohol. In tests of the sensitiveness of the method a 0·001 *N* solution of

potassium chloride containing the above proportions of alcohol gave a flocculent precipitate in 3 minutes, while with a 0·0004 *N* solution, one day was required for noticeable precipitation to occur; a saturated solution of common salt, treated as above, gave a faint precipitate in one day, indicating the presence of a trace of potassium chloride. *Quantitative.*—For quantitative purposes the precipitation is carried out in a solution containing a larger proportion of alcohol, and the reagents to be used are:—(1) 77 per cent. alcohol (4 vols. of 95 per cent. alcohol to 1 vol. of water), (2) 0·1 *N* aniline bitartrate solution in 77 per cent. alcohol. The mixed chlorides (0·15 to 0·4 grm.) are dissolved in 12·5 times their weight of water mixed with four times that quantity of alcohol (95 per cent.). The aniline bitartrate solution is added in small portions, at intervals, until no further precipitation occurs either of potassium bitartrate or of star-shaped crystals of the reagent which appear in consequence of the higher alcoholic strength of the liquid, as compared with that used in the qualitative method. After keeping overnight, the precipitate is filtered off and washed with 77 per cent. alcohol; the filter and precipitate are ashed, the residue is moistened with a few drops of concentrated hydrochloric acid, the acid is evaporated and the residue is gently ignited and weighed as potassium chloride. The sodium chloride may be determined by evaporating the filtrate to dryness and igniting the residue. Satisfactory results of three test experiments are cited in support of the method. S. G. C.

Determination and Occurrence of Iodine in Phosphate Rock. W. L. Hill and K. D. Jacob. (*J. Assoc. Off. Agr. Chem.*, 1933, **16**, 128–137.)—*Determination.*—The following dry-distillation method was employed, and was found preferable to the acid-distillation method of Glumm and Isenbruch (*Biochem. Ztg.*, 1929, **207**, 368): A 5 to 10-grm. sample (100 mesh) contained in a porcelain boat, was heated at 1000° C. for 3 hours in a silica-tube furnace in a slow stream of oxygen which had been purified by passage through, successively, a tower filled with glass wool, 40 per cent. potassium hydroxide solution, and concentrated sulphuric acid. The volatilised iodine was absorbed in 100 c.c. of potassium carbonate solution (2·5 per cent.), into which dipped the exit end of the combustion tube, which was constricted and bent downwards at right angles. After the heating, the flow of oxygen was continued until the tube had cooled to 300° C., when the boat was removed, and the inside of the tube, together with the contents of the absorption vessel, was rinsed out into a dish, the liquid was evaporated to dryness, and the residue was heated to 400° C. to char traces of organic matter. The residue was ground with a little water to yield a thick paste, which was extracted 4 or 5 times by grinding with 5 to 10 c.c.-portions of 95 per cent. alcohol, the liquid being decanted through a 5-cm. filter paper. The filtered extract was evaporated to dryness. The residue left on evaporation was dissolved in 5 c.c. of water, and 1 c.c. of saturated sulphur dioxide solution was added to reduce iodates. Dilute sulphuric acid was added in quantity sufficient to render the solution, after it had been boiled, barely acid to bromophenol blue indicator paper. The solution was boiled for 3 minutes to expel the excess of sulphur dioxide, cooled to room temperature, and filtered. The filtrate and washings were brought to a volume of 10 c.c., and transferred to a 12-c.c. separating funnel. The iodine was

liberated by the addition of 1 c.c. of sodium nitrite solution (2·5 per cent.) in the presence of 1 c.c. of carbon tetrachloride. The stoppered funnel was shaken 100 times and set aside for 1 to 2 minutes to allow the liquids to separate. The carbon tetrachloride layer was drawn off into a 1-c.c. stoppered bottle and centrifuged (3000 r.p.m.) for 3 to 5 minutes, in order to produce a clear liquid. This was compared in a micro-colorimeter with a standard iodine solution prepared in the same way from a known amount of potassium iodide solution. In tests of the method on a synthetic mixture of 0·1 mgrm. of iodine as potassium iodide and 5 grms. of iodine-free tri-calcium phosphate, recoveries of 93 and 99 per cent. of the added iodine were obtained in duplicate experiments.

Occurrence.—Some 40 different samples of phosphate rock from the U.S. and N. Africa were analysed. While iodine was found in all the samples, the proportion present varied over a wide range—from, *e.g.* 0·8 parts per million in Montana and Wyoming phosphate to 130 parts per million in one sample of Florida hard-rock phosphate. The results, in general, were 40 to 50 per cent. higher than previously published results for similar materials. A relationship is traced between the iodine content and the geological age of the phosphate deposits; thus, those belonging to the Tertiary period, especially the lower Tertiary, are richest in iodine, while Quaternary phosphates contain considerably less iodine, and Permian phosphates least of all. The various results available of the distribution of iodine in rocks indicate that iodine has accumulated to a much greater extent in phosphate rock than in other rock deposits. S. G. C.

Microchemical

Collected References to the Micro-determination of Iron in Biological Material. Z. Stary. (*Mikrochem.*, 1933, **12**, 355–374.)—References to the micro-determination of iron in biological material are collected. For the determination of total iron, methods of dry and wet ashing are described, and also a method by which the organic matter is partly oxidised and then separated from the portion containing the iron. Methods for the separate determination of iron in blood and tissues, and in hæmoglobin, are given. The easily-separated "inorganic" iron may be determined either by difference or directly, and the bi- and ter-valent iron present may also be found. The various methods for the determination of iron are given in detail. The colorimetric methods include the determination as thiocyanate and as ferrocyanide; the less common colorimetric methods with the following reagents are briefly mentioned:—Salicylic acid, α-α-dipyridyl, alloxantin, thioglycollic acid, di-*iso*-nitroso-acetone, pyrocatechol, pyramidone, *iso*-nitroso-acetophenone, dimethyl-glyoxime, acetyl-acetone, benzoyl-acetone. The volumetric methods include the potassium permanganate titration method, with zinc or mercury as reducing agent, and the iodimetric method. An account is given of the potentiometric titanium method, and of a gravimetric method in which iron is precipitated with nitroso-β-naphthol. Catalytic methods are described. References to 69 original papers are given. J. W. B.

Collected References to the Microchemistry of Aluminium, Chromium, Iron, Titanium, and Uranium. K. Heller. (*Mikrochem.*, 1933, **12**, 327–354.)—References since 1925 to methods of micro-detection and micro-determination of the metals are collected. The qualitative methods include spectrographic methods, "spot" tests, catalytic reactions and crystal formation, together with details of procedure in the presence of interfering substances, and the sensitivity of the tests. The quantitative methods include spectrographic, gravimetric, volumetric, colorimetric and radiographic methods. Descriptions are given, together with the limits of accuracy. References are given to **146** original papers. J. W. B.

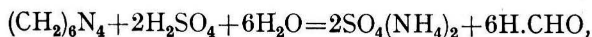
Collected References to the Micro-Detection of Cobalt, Nickel, Manganese and Zinc. K. Heller. (*Mikrochem.*, 1933, **12**, 375–395.)—References to the micro-detection of the metals are collected. The methods include electrolytic, catalytic and spectrographic methods, "spot" tests and crystal formation. Details of the methods, and the sensitivity of the tests are given. References are given to **101** original papers. J. W. B.

Micro-acidometric Method for the Determination of Nickel. J. V. Dubsky and E. Hauer. (*Mikrochem.*, 1933, **12**, 321–326.)—Nickel is determined by precipitation with dicyandiamidine, and the precipitate is dissolved in a known volume of standard hydrochloric acid, according to the equation:—

$$Ni(C_2H_5NO)_2+4HCl \rightarrow NiCl_2+2(C_2H_6N_4O.HCl),$$

methyl red being used as indicator. The method is adapted from that of J. Mika (*Z. anal. Chem.*, 1929, **78**, 268). It can be used for as little as 1·4 mgrm. of nickel, and is accurate to approximately ± 1 per cent. *Method.*—The nickel salt is dissolved in water containing a few drops of concentrated hydrochloric acid, the solution is warmed, and an excess of dicyandiamidine sulphate solution is added, followed by dilute potassium hydroxide solution until the colour turns yellow, or a yellow precipitate is formed. The mixture should stand overnight. The precipitate is filtered off on a small filter, washed with water containing a drop of ammonia, and finally with water, until the filtrate is no longer alkaline, after which it is washed with a little water into a beaker, and titrated with 0·1 *N* hydrochloric acid from a micro-burette. The precipitate dissolves during the titration, and when solution is complete the indicator turns red. It is of no advantage to use 0·01 *N* acid, as the end-point is less sharp. J. W. B.

New Method for the Micro and Semimicro-Determination of Magnesium. A. Blanchetière and M. Arnoux. (*J. Pharm. Chim.*, 1933, **17**, 97–107.)—Magnesium is precipitated by hexamethylene-tetramine in the presence of excess of potassium iodide as a complex of the formula $MgI_2,10H_2O, 2[(CH_2)_6N_4]$. The precipitate is filtered off and washed with acetone saturated with the compound, and, after being redissolved in water, it is determined in one of two ways: (i) The hexamethylene-tetramine portion of the compound is determined by titration with standard sulphuric acid according to the equation:



$$(CH_2)_6N_4+2H_2SO_4+6H_2O=2SO_4(NH_4)_2+6H.CHO,$$

1 c.c. of $N/100$ sulphuric acid corresponds with 0·0304 mgrm. of magnesium. (ii) The iodine in the compound is determined by titration with $N/100$ silver nitrate solution, 1 c.c. of which is equivalent to 0·1215 mgrm. of magnesium. This method is more suited to the semi-micro scale. METHOD (i): *Reagents*.—(1) Thirty c.c. of a cold saturated solution of hexamethylene-tetramine containing 15 grms. of pure potassium iodide. (2) Acetone saturated in the cold with the complex double iodide of hexamethylene-tetramine and magnesium; this must be kept in the dark, otherwise iodine is liberated. (3) Chloroform, saturated in the cold with the complex, and kept in the dark. This must be frequently renewed. (4) $N/20$ or $N/25$ sulphuric acid. (5) $N/100$ or $N/25$ alkali. (6) Alizarin potassium sulphonate. The precipitation is carried out in micro-beakers of 4 to 5 c.c. capacity, 2 c.c. of test solution are used, and 2·20 grms. of potassium iodide are added. The mixture is stirred with a micro-stirrer until solution is complete, then 0·9 c.c. of the hexamethylene-tetramine reagent is added. The mixture is stirred and then allowed to stand in ice for 30 minutes. A Pregl-type suction filter of Jena glass (Schott 12 G3 or 12 G4) is used. The precipitate, which is easy to filter and does not stick to the glass, is washed, each time with 0·5 c.c. of wash liquid, twice with the acetone wash liquid and 5 times with chloroform, again twice with acetone, and finally twice with chloroform. The precipitate is dissolved in 4 c.c. of boiling water, in 3 portions, the solution passing through the filter into a tube of 30 c.c. capacity containing a measured volume of $N/20$ sulphuric acid (2 c.c.) and a drop of alizarin sulphonate. The tube is heated over the water-bath for 10 minutes, after which the contents are titrated against $N/100$ alkali until the indicator changes to pink. The burette should be graduated to read 1/30 c.c. or less.

METHOD (ii): *Reagents*.—(1) Hexamethylene-tetramine reagent as above; (2) acetone saturated as above; (3) $N/100$ silver nitrate solution; (4) $N/100$ ammonium thiocyanate solution; (5) saturated solution of iron alum in concentrated nitric acid. The precipitation and filtration are carried out as before, except that only acetone is used for washing (15 c.c. in all, 1 c.c. for each washing). The final washings should be mixed with water and tested with silver nitrate. The precipitate is dissolved, as before, in 4 c.c. of water, into a tube of 30 c.c. capacity, containing 5 c.c. of $N/100$ silver nitrate solution and about 2 c.c. of the acid iron alum solution. The solution is titrated against the $N/100$ thiocyanate solution. A blank determination should always be carried out. It is essential that the precipitation be carried out in the cold, as high temperatures cause the results to be very low. Calcium may be present up to a concentration of 0·4 mgrm. per c.c.; higher concentrations, such as 2 mgrm. per c.c., may cause the results to be 20 per cent. too high. For the determination of magnesium in blood it is not necessary to remove the calcium. The presence of phosphates causes the results to be low; the effect may be reduced by carrying out the precipitation in the presence of a drop of dilute acetic acid, but may still be of the order of 10 per cent. too high, and therefore phosphates should be removed. Method (i) gives results approximately 5 per cent. too low for amounts of magnesium varying from 1·0 to 0·12 mgrm.; Method (ii) is less accurate for small amounts, and also gives results which are lower than the theoretical values. J. W. B.

Determination of Periodic Acid in the Presence of Iodic Acid. P. Fleury and J. Lange. (*J. Pharm. Chim.*, 1933, **17**, 107–113.)—(i) *Arsenious acid method.*—Periodic acid oxidises arsenious acid to arsenic acid according to the equation:—$2HIO_4+As_2O_3=2HIO_3+As_2O_5$. The reaction is carried out in solution in the presence of excess of sodium bicarbonate, and when the reaction is complete the unoxidised arsenious acid is determined by titration with iodine. The reaction is very slow, but is much more rapid in the presence of iodide. For each determination 5 to 25 c.c. of periodate solution, neutral to phenolphthalein (representing about 5 to 6 c.c. of 1/10 molar periodic acid, and capable of oxidising 10 to 12 c.c. of *N*/10 arsenious acid) are mixed with 5 to 10 c.c. of a saturated solution of sodium bicarbonate (approximately 8 per cent.), then 15 c.c. of a *N*/10 arsenious acid, containing bicarbonate, and finally 1 c.c. of a 20 per cent. solution of potassium iodide. After 15 minutes at laboratory temperature the excess of arsenious acid is titrated against *N*/10 iodine solution. Results are accurate to within 1 or 2 per cent. (ii) *Manganous carbonate method.*—When an excess of sodium carbonate is added to a solution containing periodic acid and manganous sulphate, the periodic acid is reduced to iodic acid, while the manganous carbonate (which precipitates) is oxidised. The precipitate is collected, washed, and treated with an acid solution of potassium iodide, and the iodine liberated is titrated with sodium thiosulphate solution. All the operations are carried out in a centrifuge tube of 40 c.c. capacity and the precipitate is separated by centrifuging. A blank test should be made. The amounts of reagent solutions used for 10 c.c. of periodic acid solution (representing 3 c.c. of *M*/20 periodic acid) are:—Three c.c. of sodium hydroxide solution (14·3 per cent.), and 10 c.c. of a 1 per cent. manganese sulphate (anhydrous) solution. After 4 or 5 minutes the mixture is centrifuged, and washed 3 times with 5 per cent. sodium sulphate solution. Then 2 c.c. of 20 per cent. potassium iodide solution and 0·4 to 0·5 c.c. of 20 per cent. (by volume) sulphuric acid are added. The liberated iodine is titrated with sodium thiosulphate solution by means of a burette graduated in 1/20 c.c. The method is suitable for amounts varying from 10 to 100 mgrms. of periodate, with an experimental error of 3 per cent. J. W. B.

Physical Methods, Apparatus, etc.

Metal-connected Glass Electrode. M. R. Thompson. (*Bur. of Standards Research Paper No.* 511, *Jour. of Res.*, 1932, **9**, 833–853.)—The advantages of the glass electrode include freedom from disturbance by many electrode poisons and by oxidation-reduction potentials, and elimination of the use of hydrogen or quinhydrone. On the other hand, it necessitates the use of special electrical measuring-instruments on account of its high resistance, and it is very fragile. The author has overcome these disadvantages by means of a glass electrode with a relatively thick wall, a metal connection being made directly to the glass; this arrangement also eliminates one of the standard electrodes normally required. The best results were obtained by silvering the outer or inner surfaces of test tubes 0·5 mm. thick, 1·2 cm. in external diameter and 12 cm. long, with Rochelle salt (cf. *Bureau of Standards, Circular No.* 389, 1931), this layer being then plated

with a deposit of copper about 0·008 mm. thick. A copper wire was held fixed in contact with the metal coating, and the tubes were then coated with paraffin wax to diminish surface-leakages. Simple application of a layer of tin-foil was also found to be satisfactory. The container pattern of electrode gave more accurate results than the dipping type. In one case where the metal was insulated from the glass by an air-gap, thus producing a resistance of 5000 megohms, the results were accurate to within $\pm 0{\cdot}5\, p_H$; this suggests that electrode action does not necessarily require actual contact between metal and glass, completion of the circuit being effected probably either by surface-leakage or by induction. Comparative measurements against other electrodes and the usual type of glass electrode are given for a number of buffers and electrolytes, and graphs relating the p_H value and the observed voltage are shown for a p_H range of -3 to $+15$ in each case. The results show that the new electrode compares very favourably with the older type so far as range, ageing effect, salt and protein errors, and effects of poisons are concerned. Gelatin, moderate concentrations of salts of the alkali metals, and low concentrations of salts of the heavy metals produce small errors, but oxidation-reduction potentials have little, if any, effect. It is suggested that equilibrium between hydrogen ions on the opposite sides of a glass wall is not essential to the functioning of the glass electrode, and that deep penetration of such ions into the glass may not occur. J. G.

Application of Infra-red Photography to Textiles. P. W. Cunliffe. (*J. Soc. Dyers and Col.*, 1933, **49**, 73.)—In photographing textile materials with infra-red rays, the object is focussed in white light, and a special filter (obtainable from the makers of the plates) is placed before the lens or before the source of light, which during exposure should be rich in infra-red rays, *e.g.* electric lamp, gas or oil lamp, and the aperture should not be larger than f. 11. Special plates are required (obtainable from Ilford, Ltd.), and these are developed by the time-temperature method in total darkness after trial exposures. The speed of the combined filter and plate is about 100 H. and D. to artificial light, and 10 H. and D. to daylight. A photograph is shown of a dark blue bathing suit which, although quite even to the eye in shade, was found to bleed in an unusual manner. A regular series of bars not shown in an ordinary photograph was revealed by infra-red photography. It was found that the portion giving the bars was dyed with a different dye from the remainder. A further possible use of the method is for the selection of dyestuffs for dark cloths, which are to be as cool as possible in summer (O. Bloch, *Photographic J.*, 1932, **72**, 334). A range of dyeings photographed by infra-red rays is given. R. F. I.

Reviews

The Extra Pharmacopoeia of Martindale and Westcott. Revised by W. H. Martindale, Ph.D. Twentieth Edition, in two volumes. Vol. I, pp. xlviii+1216. London: H. K. Lewis & Co., Ltd. 1932. Price 27s. 6d. net.

Any book which has reached its twentieth edition and its jubilee year may be regarded as by way of being an institution. That the work under review is an institution not lightly to be regarded is shown by the fact that the Commissioners of Customs and Excise are prepared to consider articles made in accordance with formulae contained therein as known, admitted and approved remedies for the purposes of the Medicine Stamp Act.

As it is impossible to contemplate the rise of a generation which knows not "Martindale"—one has at least that much faith in human nature—it is unnecessary to speak in very great detail of its contents. It is interesting to recall, however, that the first edition, published in 1883, contained a mere 313 pages, whilst the thirteenth, published in 1908, contained over 1200. The next edition of the book was divided into two volumes, the analytical part being contained in the second volume, and the whole work running to some 2000 pages.

The work as a whole is intended for medical men, pharmacists, and analysts. The volume under review is primarily intended for the two former classes, but all analysts who have to deal in any way with drugs will find much of interest and value in its pages. All the Pharmacopoeial drugs are described and, in addition, many hundreds of others, some of which have established reputations and others of which are more or less in the experimental stage; it may, in fact, be regarded as a synopsis of current medicine. In addition, there are very full abstracts of the laws relating particularly to medicine and pharmacy.

It is, of course, quite impossible to deal at all adequately with the mass of information provided. The index alone runs to 100 double-column pages, and the therapeutic index, giving suggested remedies for diseases and symptoms, extends to over 73 pages of small type. When one thus sees in print some hundreds of diseases from which it is possible to suffer, one is left wondering by what miracle ill-health or premature death can possibly be avoided by anyone.

The 1932 revision of the British Pharmacopoeia has not yet been incorporated into the text, a fact that is not surprising seeing that the preface is dated September 29th, 1932, but a complete synopsis of the principal additions and changes, grouped together in a very convenient manner, is included in the introduction.

The present edition is uniform in appearance with its forerunners, and, in spite of the fact that it contains a few more pages, the thickness has been reduced by about one quarter. One of the main characteristics of the earlier editions has been the remarkable manner in which the book has been kept right up-to-date; the present edition carries on this tradition right worthily, and is to be thoroughly recommended to all those who have anything to do with the subjects treated in its pages.

G. D. Elsdon

ORGANIC REAGENTS FOR METALS. The Staff of the Research Laboratory of Hopkin & Williams, Ltd. Pp. 60. Price 1s.

Organic reagents for the detection and estimation of metals have become important because of the increased attention paid to the effect of traces of metals not only on chemical and biological reactions, but also on industrial processes and on the appearance and keeping qualities of foodstuffs, textiles and many other commercial products. Messrs. Hopkin & Williams have performed a very useful service to analysts by supplying this monograph, which contains a description of 18 of these compounds, together with working details for their use in the detection and estimation of 22 metals. Useful bibliographies relating to each of the compounds described are also included. One small error is noticeable. Cazeneuve's reagent for chromate (diphenylcarbazide), although its M.W. is quoted correctly, has been given the formula of diphenyl-semicarbazide. Yoe (*Photometric Chemical Reactions*, Vol. I) states incorrectly that diphenylsemicarbazide is Cazeneuve's reagent. Both compounds give a violet-red colour with chromates, but diphenylcarbazide is the better reagent because it is more soluble in dilute acetic acid than the sparingly-soluble semicarbazide. H. PHILLIPS

COLORIMETRY: ITS APPLICATIONS IN ANALYTICAL AND CLINICAL PRACTICE. HUGO FREUND. Translated by F. BAMFORD. 8vo, pp. 255. Published by the Author. Sold by E. Leitz (London), 20, Mortimer Street, W. 1. Price 10s.

In recent years there has been a considerable extension of methods for the determination of traces of substances in which the measurement of colour plays a part. The colorimetric methods for the determination of hydrogen ion concentration have also extended the field of such measurements. A good colorimeter may, in fact, be said to be almost a necessity in the modern analytical laboratory. These instruments have been recently much improved, and it is now possible to obtain at a fairly reasonable cost colorimeters which are a delight to handle. Indeed, the apparent accuracy of colour comparisons in these instruments may easily lead the unwary analyst to entirely unwarranted assumptions as to the accuracy of some colorimetric methods. Apart from the personal errors always present in colorimetric measurements, the method used for the production of the colour is frequently liable to errors, and very slight differences in technique may be the cause of serious variations. The use of the photo-electric cell has been suggested as a means of eliminating the personal factor, especially for unstable colours, and one may expect developments in this direction in the future.

Nevertheless, there are many valuable and accurate colorimetric methods available, and one approaches a book which is confined to them with a considerable degree of hopefulness. The author states in his preface that "the book cannot lay claim to absolute completeness." Since the book attempts to cover almost the whole field of chemical analysis it is clear from its size that this cannot be so, and, indeed, no one wants a book which is merely a compilation of all the published methods, good or bad. The number of processes which have been published for the colorimetric determination of adrenaline, for example, runs well into double figures, but only one (Folin's method) is given here, and this, though sometimes useful, is not specific for adrenaline.

Such valuable colour tests as the antimony trichloride reaction for oils containing vitamin *A*, the Smith and Van Urk test for ergot alkaloids, Radulescu's test for morphine, and the determination of lead as sulphide in alkaline solution (to mention only a few) are ignored. (The method given for lead in water is carried out in acid solution and would include copper as well.)

The book is divided into sections on Instruments, Hydrogen Ion Concentration, Biochemistry, Medicine, Food Chemistry, Agricultural Chemistry, Water Analysis, and Metals.

A brief description is given of the Duboscq colorimeter, with the extensions of this principle embodied in the Bürker, the Leitz Universal, and the Leitz Compensating Colorimeters. No description is given of wedge colorimeters, such as the Hellige instrument and its various modifications, or of the Lovibond tintometer.

The section on hydrogen ion concentration is based entirely on the use of the Leitz Compensating Colorimeter. Doubtless this is an excellent method, but the chapter will be of little use to workers who do not possess the instrument.

The section on Colorimetry in Biochemistry includes only methods for the determination of peroxidase and the quantitative analysis of the "constituents of chlorophyll." The latter apparently include carotene and xanthophyll, but the actual separation is not described, presumably because the author finds the method too long for inclusion, and gives only a reference to the original paper.

The section on Colorimetry in Medicine, by which is meant chiefly the examination of blood and urine, is the most extensive and probably the best in the book. For the determination of traces of mercury in urine Stock's method, involving the use of diphenylcarbazide, is mentioned, but no reference is given to later papers which show that the colour given is due to diphenylcarbazone in the diphenylcarbazide, and that therefore diphenylcarbazone is a better reagent for the test, since the interference of certain other metals is thereby avoided. One looks in vain for Folin's colorimetric ferricyanide method for the determination of blood sugar, but his earlier copper colorimetric method (which he has now abandoned) is given. Czonka's original method (1916) for the colorimetric determination of acetone in urine is given, but no mention is made of the improvements in this method effected by Behre and Benedict in 1926.

Examples such as these (and there are many others), coupled with the absence of references later than 1928 (except one added by the translator), impress upon one that, in reviewing this book, it is useless to take into consideration any work published in the last five years. Considering the great advances which have been made during that period in colorimetric methods, the book cannot be recommended as exactly up to date. But, even if one dismisses from one's mind the work of the last five years, the general impression left is that the book is a collection of methods, not on the whole very well described, and put together without the exercise of a very acute critical faculty.

The book is well printed and typographical errors are rare, but there is no index. The omission of the final "e" results in such words as tyrosin, cystin, pepton, creatinin, which are not usual in this country; otherwise the translator appears to have done his part well.

NORMAN EVERS

THE GENERAL PROPERTIES OF MATTER. By F. H. NEWMAN, D.Sc., and V. H. L. SEARLE, M.Sc. Second Edition. Pp. 388. London: Ernest Benn, Ltd. 1933. Price 18s.

This work was first published in 1929, and the fact that a second edition should now be required is sufficient evidence of its widespread adoption. Although it was originally intended to be a text-book, giving a fundamental treatment of the properties of matter for students of physics, it will be of considerable use in the hands of chemistry students who desire to obtain a sound grounding in the principles underlying such properties as surface tension, viscosity, the kinetic theory of matter and osmotic pressure, which are assuming increasing importance in the study of physical chemistry. In this respect it will serve as a useful adjunct to the standard works on physical chemistry. The book is clearly and concisely written. An elementary knowledge of the calculus is assumed.

Mention should also be made of the reduction in price which has been made for this edition.

H. T. S. BRITTON

ANALYTICAL FACTORS AND THEIR LOGARITHMS. E. R. CALEY. Pp. 112+v. New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. 1932. Price 12s. 6d.

This little book has been compiled for the express purpose of supplying the analyst with a comprehensive set of chemical factor tables that will enable him to perform quickly the calculation which the actual experimental data must always connect with the desired information. The factors are based on the International Atomic Weights of 1931.

In all, eleven tables are given, and in them will be found data for all the common gravimetric and volumetric processes. In the former case the generally accepted temperature for the drying or the ignition of the precipitate has been inserted—a feature which is rare, if not unique, in books of this kind. A table of special interest is one for estimations involving the use of the newer organic reagents for metals, such as 8-hydroxyquinoline, 6-nitroquinoline, "nitron," benzoyl-methyl-glyoxime, 6-chloro-5-nitro-*m*-toluene sulphonate, etc. In this table original references are given. The book concludes with a very legible set of 5-figure logarithms and instructions for the use of the tables in general.

The author has succeeded in his aim with regard to comprehensiveness, and therein lies the usefulness of his book, but for many an analyst who would gladly use it, the price is, we venture to think, excessive.

HAROLD TOMS

ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY. 1932. Vol. XVII.

The Society of Chemical Industry is once again to be congratulated on the publication of its Annual Report, which fully maintains the high standard set by its predecessors. Its twenty-six chapters cover every aspect of applied chemistry, from chemical engineering to vitamins, from dyestuffs to agriculture, and from metallurgy to photography. All the articles are written by specialists in the

relevant branches of chemistry; thirty-seven authors have collaborated in the Report. It is impossible for anyone to review their work in detail, since it is itself a compilation of reviews. All that can be done is to record a general impression.

The book is very readable and of great interest, for it keeps the chemist in touch with progress in the many sections of chemical industry with which he himself may not be conversant. The outlook of applied chemistry is to-day rapidly widening, and it is more important than ever for the individual chemist to keep himself familiar with branches outside his immediate activities. The authors must have been faced with an arduous task in collecting and sorting the information given in the book, and it appears that very little, if anything, of importance has been omitted.

The book contains complete author and subject indexes and a comprehensive bibliography. It is printed and bound in a form identical with that of its predecessors. Those who possess the earlier volumes will need no advice to obtain this one; those who do not possess the earlier volumes will wonder how they can have managed without them when they have obtained this one, and their library will certainly not be complete unless they do so.

S. G. STEVENSON

INDUSTRIAL MICROSCOPY. By W. GARNER, M.Sc. Pp. vii+389. London: Sir Isaac Pitman & Sons, Ltd. 1932. Price 21s. net.

This book is an ambitious venture, for each of its chapters is a separate treatise on the use of the microscope or on the technique of its application to various branches of industry. Although every analyst is presumed to have had a training in microscopy, many fail to get the best out of the instrument through lack of knowledge of detail such as the author here supplies.

The introductory chapter, which deals with the construction of the microscope and the choice of objectives and their correction, is essentially elementary—perhaps almost too much so. Then comes a useful chapter on general technique, including the methods of illumination and the use of colour screens, and in the third chapter there is a description of various accessories such as the spectroscopic eyepiece, polarising attachments (with a section on the behaviour of crystals in polarised light), and an outline of ultra-microscopy. Chapter V is concerned with measurement, counting and drawing, and Chapter VI with the technique of photomicrography; both are thoroughly practical, one of the sections giving an admirable account of the control of contrast.

Chapters VI, VII and VIII form a concise introduction to micro-chemistry, dealing practically with the general technique, the determination of physical constants, and the detection and determination of inorganic and organic substances, and include routine schemes of analysis.

The next two chapters describe the methods to be used in botanical investigations, and give an account of botanical structures. Chapter XI deals at some length with the examination of textiles and paper fibres, but omits to refer to the valuable work of Dickson on the differentiation and determination of paper

fibres by the use of polarised light. Insects and allied organisms (moths, beetles, mites) of industrial importance, form the subject-matter of Chapter XII. Then come chapters on bacteriological technique, bacteria (with a discussion on their classification), fungi and their classification, and the examination of water and sewage, and the last chapter (XVII) consists of a collection of formulae of microscopical reagents, photographic developers, inks for special purposes, and the like.

The book is well illustrated throughout, has a comprehensive bibliography at the end of each chapter, and is efficiently indexed. Its author has aimed at producing, not a manual of microscopy, but a guide to the microscopical examination of the raw materials and the products of industry, and in this aim he has succeeded so well that his book should find a welcome among all whose work involves the use of the microscope.

EDITOR

Publications Received

THE CONDUCTIVITY OF SOLUTIONS. Second Edition. By C. W. DAVIES. London: Chapman & Hall. 1933. Price 15s. net.

LUBRICATING AND ALLIED OILS. By E. A. EVANS. London: Chapman & Hall. 1933. Price 9s. 6d. net.

BASIC GERMAN FOR SCIENCE STUDENTS. By M. L. BARKER. Cambridge: W. Heffer & Sons, Ltd. 1933. Price 6s. net.

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

PHYSIKALISCHE METHODEN DER ANALYTISCHEN CHEMIE. Erster Teil. By E. SCHEIBE, H. MARK and R. EHRENBERG. Leipzig: Akademische Verlagsges. m.b.H. Price M.36.

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THE HISTORY OF THE MICROSCOPE. By R. S. CLAY and T. H. COURT. London: Ch. Griffin & Co., Ltd. Price 30s.

CONTESTED DOCUMENTS AND FORGERIES. By F. BREWESTER. Calcutta: The Book Co., Ltd. Price Rs. 16-8.

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