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The Action of Natural Waters on Lead.

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(Read at the Meeting, June 7, 1922.)

PART I. EFFECT OF VARIOUS SALINE CONSTITUENTS.

IN a paper contributed to the Society of Public Analysts, and published in the ANALYST (1921, 46, 270), it was shown: (1) That pure water had no action upon lead; but that (2) in the presence of oxygen, action did take place, lead oxide or hydroxide being formed and remaining in solution in a colloid condition, the liquid having an alkaline reaction.

In pure water supersaturated with oxygen the oxidising action continues until the whole of the oxygen is taken up; and if more hydroxide is formed than the water can retain in solution, it is deposited in an indefinitely crystalline condition. When, besides oxygen, carbonic acid is present, this combines with the oxide, and bicarbonate, carbonate or oxycarbonate of lead is formed; and if the oxygen is in excess, oxycarbonate and hydroxide are the final products. The effect of temperature and of agitation were also referred to, and also the difficulty of ascertaining the amount of lead in actual solution.

CONDITION OF LEAD IN WATER.—In a water with an acid reaction, or rather with a hydrogen ion concentration represented by $P_{\text{H}} = +7$, lead may occur in molecular solution and be capable of accurate estimation. If kept for a period, the amount remains constant. With $P_{\text{H}} = -7$ it is possible that at least a portion of the lead compound is in a colloid condition, tending to form molecular aggregates,

which may render the solution first opalescent, then turbid, and finally cause a definite precipitate. For example, in some cases where the water poured off at the end of the 24 hours' contact with lead has contained several mgrms. of lead per 100 c.c., and had an alkaline reaction, the amount of lead has gradually decreased upon standing, until the water was practically free therefrom; but since each time the bottle is opened a little air (with carbon dioxide) gains access, there is a question whether this carbon dioxide may not be responsible for the deposition of the final fraction. The following are the results of an experiment with a pure distilled water which had been poured over clean chalk, (a) once, (b) twice, and (c) thrice. The amounts of the constituents are parts per 100,000:

	(a)	(b)	(c)
Electric conductivity.. ..	47°	68°	94°
Approximate P _H	9	9	9
Oxygen lost in 24 hours	0.906	0.857	0.847
Lead in decanted solution	8.33	8.3	5.1
„ 24 hours later	4.04	2.4	2.1
„ end of 6 days	2.9	1.05	1.2

The liquid was faintly opalescent at the end of 24 hours in each case, and did not become absolutely bright for a week. The clarification of the solution, from above downwards, could easily be traced.

In many cases the addition of fresh hydrogen sulphide water to the liquid, drawn off at the end of the 24 hours' contact with lead, causes little or no coloration, whilst with the *previous* addition of acetic acid gelatin solution the presence of lead in considerable quantity may be indicated (*loc. cit.*). The addition of the acid *after* the hydrogen sulphide has no effect in these cases, indicating that the lead present has already been converted into sulphide, and this not being in the colloid condition, no appreciable colour has been produced. A point, which will be seen later to be of importance, is that the addition of a little alkaline citrate or tartrate to such a solution has a similar effect to the addition of acid, the hydrogen sulphide added to the alkaline solution showing that lead is now in solution. It may also be noted here that a dilute solution of lead subacetate, which, if added to distilled water, causes a turbidity, remains quite clear when a little citrate or tartrate is present. It is quite certain that there are substances of organic origin in peaty waters, or waters containing organic matters, which have some effect on the solubility of lead salts, and which are of great importance in affecting the action of moorland waters on lead.

In Table I. (p. 464) it does not follow that the expression "lead in liquid" implies that the lead is all in molecular solution, nor does it follow that a repetition of the experiment will give exactly the same results for the "lead in suspension" and "lead on foil." A water which has not been agitated during the 24 hours' experiment will give a smaller amount of "lead in suspension" and a larger amount of "lead on foil" than a sample which has been shaken from time to time. The character of the distilled water used for making imitations of natural waters may also affect the results, and latterly the only distilled water used has had an electric

conductivity of 2° at 20° C. and a P_H value of 6.5 to 7, and every sample has been tested immediately before use.

PREPARATION OF CONDUCTIVITY WATER.—By adopting the following process a quantity of distilled water with E.C.1 can be obtained by a single distillation: Select a water containing a mere trace of carbonates; a very clean rain water suffices. Estimate the amount of *N* acid required to neutralise 1 gallon. Add a trace more than this of sulphuric or citric acid and boil gently for ten minutes to drive off all the carbon dioxide. Then add a solution of sodium silicate (free from carbon dioxide) until the liquid is just alkaline to bromthymol blue. Continue the boiling for some minutes; then connect the flask with the condenser and distil. Estimate the E.C. from time to time. With the apparatus used about 1 litre could be collected with E.C.1 and 2 litres with E.C.2. This apparatus consists of a gallon tinned copper vessel, with which is connected an eight-bulbed Young's dephlegmator and a metal Davies' condenser. The distillation is conducted slowly, and the distilled water collected without access of air containing carbon dioxide.

Unless otherwise stated, all the experiments recorded in this paper were made by placing lead foil 6.5 by 3 cm. in stoppered bottles holding 130 c.c. of the water to be examined, three bottles being used for each examination. Bottle No. 1 was used for estimating the oxygen present in the water. In this no lead had been placed. The others, containing lead foil, were securely stoppered and water-sealed, and kept at as uniform a temperature as possible for 24 hours, and during the first 12 hours they were shaken from time to time. They remained at rest for the remaining 12 hours; the stoppers were then removed quickly, the condition of the liquid and of the lead foil having been noted, the residual oxygen estimated in one, and the contents of the other used for determining the P_H and the lead in the liquid and the lead deposited as a precipitate, or as a more or less transparent coating, on the glass. In many instances the total lead oxidised was estimated, but it was found to be quite unnecessary, as the amount was more accurately calculated from the oxygen removed from solution. If the lead foil appears to remain unchanged, it does not follow that there is not a deposit upon it; and if the liquid appears quite bright, it does not follow that there is not a deposit of some lead compound on the glass, which can be rendered visible by pouring out the solution, rinsing the bottle with a little distilled water, and then drying it.

In practically all the experiments on the action of acids and salts one litre of solution was prepared. Three of the 130 c.c. bottles were then filled, and the remainder tested for P_H electric conductivity, free carbon dioxide, etc.

ESTIMATION OF P_H VALUES.—Without the electric conductivity meter accurate results would have been impossible in making imitation natural waters, and it was also found that litmus, lacmoid and other similar indicators were useless for comparative purposes. A set of indicators enabling the P_H from 4 to 10 to be determined within about 0.5 appears to answer every purpose. The table appended explains how the values of P_H have been obtained.

ESTIMATION OF P_H IN DRINKING WATERS.Value of P_H .

- 10 Gives dark red with phenolphthalein.
- 9 Pink with phenolphthalein and purple red with cresol red.
- 8.5 Doubtful tint with phenolphthalein; purple red with cresol red.
- 8 No col. with phenolphthalein, red with cresol red.
- 7.5 Doubtful red with cresol red, blue with bromthymol blue.
- 7 Blue-green with bromthymol blue.
- 6.5 Green with bromthymol blue.
- 6 Yellow with bromthymol blue and with methyl red.
- 5.5 Orange with methyl red.
- 5 Orange red with methyl red; yellow with methyl orange.
- 4.5 Dark red with methyl red; and orange with methyl orange.
- 4 Orange red with methyl orange.
- 3.5 Red with methyl orange or dark orange red.
- 3 Dark red with methyl orange.
- 2 Red with methyl orange and orange with thymol blue.
- 1 Purple with thymol blue.

NOTES—7=True neutrality of water; 4= P_H of N/10,000 HCl; 3= P_H of N/1000 HCl; 2= P_H of N/100 HCl.

CLASSIFICATION OF DRINKING WATERS.—According to the hydrogen ion concentration drinking waters may be divided into three classes: (1) Those which contain carbonates and bicarbonates, but no free carbonic acid. (2) Those which contain no carbonates, but may contain bicarbonates, with or without free carbonic acid. (3) Those containing neither carbonates nor bicarbonates, but which may contain a free acid besides carbonic acid.

The first group gives a red coloration with phenolphthalein and purple with cresol red. The only waters of this type are those resembling the water from the Thanet Sands in Essex and London, which contain bicarbonates and traces of carbonates but no free carbon dioxide.

The second group contains the great majority of waters. The P_H exceeds 4.5, and, upon boiling, the free and semi-combined carbon dioxide is given off, and the P_H usually becomes about 7 to 9.

The third group is one which is rarely met with. It gives P_H 4.5, or under, and the value is not markedly affected by boiling. These waters contain some free acid other than carbonic acid. So far I have only met with such waters from moorlands near manufacturing towns, but one was derived from a shallow well on a sewage farm.

METHODS OF EXAMINATION.—Waters belonging to the different groups were examined in the following way, N/22 hydrochloric acid and N/22 sodium carbonate (corresponding to 1 mgrm. CO_2 per c.c.), being used in all cases:

GROUP 1. Titrate 100 c.c. with acid and methyl orange, No. of c.c. = a .
 then " " " " and phenolphthalein, " " = b .
 $2b = CO_2$ corresponding with base as carbonate, and
 $2(a - 2b) = CO_2$ " " " bicarbonate.

GROUP 2. Titrate 100 c.c. with sodium carbonate and phenolphthalein.

No. of c.c. = a .

 " " " acid and methyl orange. " " = b .
 a = mgrms. free CO_2 . $2b$ = mgrms. of CO_2 as bicarbonate.

GROUP 3. Titrate 100 c.c. with sodium carbonate and phenolphthalein.

No. of c.c. used = a .

100 c.c. in the same way after boiling
 gently for 5 minutes and
 cooling.

" " " = b .

$(a - b)$ = free CO_2 present. $b/2$ = equivalent of non-volatile acid present.

By comparing the P_H with the amount of free acid present, as ascertained by titration, an indication of the nature of the acid can be obtained. In all the moorland waters examined the indications are that it is of organic origin.

When a certain number of moorland waters had been collected it was found that they differed greatly in their action on lead under the conditions of the experiments, and that these differences could be divided into three classes:

- (1) Difference in amount of lead oxidised. Some samples oxidised many times more lead than others.
- (2) Difference in visible action. Some acted like pure distilled water to which a little carbonate had been added, becoming turbid in a few minutes. Others caused no turbidity whatever.
- (3) Difference in the amount of lead retained in solution. Whilst 100 c.c. of an aerated distilled water under ordinary conditions of the experiments take into solution some 11 or 12 mgrms. of lead, very few of the moorland waters retained 1 mgrm. of lead in solution.

EFFECT OF VARIATION OF CONSTITUENTS.—Before proceeding to the examination of natural waters, the action of varying quantities of possible constituents was determined. These experiments were so numerous that a few of the results only can be recorded, and those made with hydrochloric acid and sodium chloride may be given in some detail, as they exhibit certain points of interest.

When the acid present is not sufficient to combine with the whole of the lead oxidised, the liquid acquires an alkaline reaction in the presence of the most minute trace of carbonic acid, and in the process becomes dull. With an excess of acid the liquid remains clear and bright and the reaction continues acid. No. 5 is the sample of distilled water used in experiments 1 to 9 for comparison. Sodium chloride, in the quantities present in surface waters, does not prevent or retard the oxidation of the lead, but it tends to cause some of the lead salt formed to be deposited on the foil, especially when a little carbon dioxide is present. With a water which had been freed from carbon dioxide by boiling, experiment No. 10 showed in 24 hours that all the lead oxidised was in solution, but in 40 hours more than half had deposited upon the foil.

TABLE I. ACTION OF HYDROCHLORIC ACID AND SODIUM CHLORIDE.

No.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
Carbon dioxide ..	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.0	0.0
Hydrochloric acid (0.1 N) ..	0.2	0.5	1.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sodium chloride, mgrms ..	0.0	0.0	0.0	0.0	0.0	1.0	2.0	2.75	5.0	3.2	3.2
Time of action, hours	3	3	3	12	12	12	24	12	24	24	40
Original oxygen ..	1.12	1.12	1.12	1.00	0.95	1.05	0.95	0.95	0.95	0.98	0.98
Oxygen lost ..	0.48	0.53	0.56	0.98	0.93	0.675	0.91	0.685	0.87	0.84	0.74
Lead ..	6.2	6.9	7.25	12.65	10.05	8.75	11.8	8.85	11.25	10.85	9.58
Appearance, liquid ..	T	D	C & B	D	D	C & B	D	D	T	D	D
„ deposit	Nil	Nil	Nil	Nil	Slight	?	tr	?	tr	Nil	Nil
„ foil ..	N	N	N	N	Dull	N	Dull	Dull	Dull	Dull	Steely
Lead in liquid ..	6.5	7.0	7.2	11.8	8.0	5.0	—	3.0	1.2	10.8	4.4
„ deposit ..	—	—	0.0	—	2.75	0.7	—	0.8	3.0	0.0	0.0
„ on foil ..	0.0	0.0	0.0	0.85	1.3	3.05	—	5.05	7.05	0.0	5.15
Reaction of liquid ..	Alk.	Alk.	Acid.	Neut.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.	Alk.

NOTES—All in parts per 100,000, except vol. solutions, which are in c.c. per 100 c.c.

N=Normal appearance unchanged; C & B=clear and bright; D=dull; T=turbid.

Where there was no obvious precipitate, but the liquid was dull, the quantity of lead found includes any little in suspension.

The three important points brought out are that in quantities such as are found in moorland waters (a) the chlorides do not retain carbonate of lead in solution, (b) they do not retard the oxidation of the metal, and (c) they do tend to cause a deposition of some insoluble chloride on the lead foil.

Sulphuric Acid and Sulphates.—In the presence of sulphates or sulphuric acid an insoluble sulphate is formed, and the amount of lead deposited varies somewhat. A semi-transparent film is formed on the sides and bottom of the containing vessels in most cases. A litre of distilled water, to which 0.5 c.c. of 0.1 N sulphuric acid per 100 c.c. had been added, was used for filling five bottles. After standing in contact with the water for 48 hours the lead was removed, and the solutions examined. These were alkaline to cresol red (P_H 8), but not to phenolphthalein. All were clear and bright, but the lead in solution varied from 3.4 to 7.5 mgrms., and the lead adherent to the glass varied from 0.0 to 1.1 mgrm. There was no visible precipitate, but the glass was dull, and the lead-foil white. In all cases where the experiment was tried the lead in the liquid decreased daily upon standing, sometimes a barely perceptible trace being left in solution after 48 hours.

Sulphates therefore have no very marked effect in retarding the rate of oxidation of the lead unless present in substantial quantities. In all cases a considerable amount of lead is found in the liquid at the end of 24 hours, but the amount decreases upon standing. The small quantity of sulphate which occurs in moorland water in presence of other salts may have some effect on the rate of oxidation of lead, but does not prevent the formation of oxycarbonate, nor retain it in solution.

Carbonic Acid and Carbonates.—A pure oxygenated water containing more than 0.1 pt. carbon dioxide per 100,000 becomes turbid (sheeny) in a very few minutes after the lead has been introduced; with more carbon dioxide the visible action seems to be retarded; and with still more the liquid may remain clear and bright, yet much lead be oxidised and converted into a very insoluble oxycarbonate, which remains firmly adherent to the foil. With traces of carbonate (of calcium, magnesium or sodium) the solution becomes opalescent (milky), clears very slowly, and if oxygen is in excess, lead hydroxide will be found in solution. With the carbonate in excess, if the liquid is allowed to stand, the amount of lead present decreases, and the water when apparently clear, may give no indication of any lead being in solution when tested with hydrogen sulphide or ammonium hydro-sulphide; yet if acetic acid is previously added, an appreciable amount of lead is found to be present. It is obviously not in a state of molecular dispersion.

With an excess of carbonic acid, an appreciable amount of lead is found in solution, but the oxidation is little, if at all, retarded, and most of the oxidised lead is deposited on the foil. Carbonates and bicarbonates do not retard oxidation, but they form very insoluble compounds with the lead oxidised, and as the amount of carbonate increases, the amount of lead carbonate deposited on the foil also increases, whilst the amount remaining as a precipitate or suspended in the water decreases. After a time the coated lead resists the further action of the water, but it may be acted upon by any acid water. It will be found, however, that the variation in the amount of carbonates in moorland waters fails entirely to explain the differences in the action of these waters on lead.

Nitric and Nitrous Acids and their Salts.—These do not appear to have any action different from that of other acids producing soluble lead salts, but with long digestion with a nitrated water a trace of nitrous acid or of a nitrite is produced. Nitrates, especially ammonium nitrate, appear to accelerate the rate of oxidation in the early stages, but all the experiments made show that in the quantities present in moorland waters these substances have no significance.

Formic, acetic and benzoic acids are also apparently negligible, even if present in a water. Certainly they never occur in such quantities as to be worth further consideration, as they neither retard oxidation nor retain carbonate of lead in solution. *Phosphates* have a marked action when present in appreciable amounts (but not in the infinitesimal quantity found in moorland waters), producing a liquid which refuses to clarify, whilst the precipitate is comparatively difficult to dissolve.

Citric, Tartaric and Quinic Acids and their Salts.—The alkali salts of these acids in exceedingly dilute solutions possess the property of preventing the precipitation of lead carbonate, as formed when the metal is being acted upon by water containing a little free or combined carbon dioxide, and the presence of salts of this nature explains why certain waters, after acting upon lead, remain clear and bright and retain lead in solution. The effect is easily demonstrated by adding a droplet of a clear dilute solution of lead subacetate (*a*) to a sample of ordinary distilled water, and (*b*) to the same water containing about 1 mgrm. of citric acid

or sodium citrate. The former will immediately become turbid, whilst the latter will remain clear. If the water contains only a trace of free carbon dioxide, the precipitate will be shoeny and most visible in directly transmitted light, whilst if it contains a trace of a carbonate the liquid will be milky and exhibit a faint bluish opalescence.

Quinic acid, though present in leaves and stems of bilberry plants and of heather, has apparently a much less effect than citric or tartaric acid. The two latter are about equal in their action, and 1 mgrm. of either has fully the effect of 3 mgrms. of quinic acid. Humic acid does not possess the property of preventing the precipitation of lead carbonate.

These acids are worthy of especial mention, as without their aid the action of most moorland waters on lead could not be imitated in artificially prepared waters. By aid of one of these acids probably all natural waters can be imitated. The presence of such an acid was suggested when examining a Derbyshire water which was distinctly acid after boiling off the little carbon dioxide present. It was found that the organic residue contained a salt and a free acid which, when the small amount obtained was examined, suggested the presence of a citrate or tartrate, the substance more nearly resembling citrate than tartrate.

Experiments made with citric and tartaric acids and their salts showed that the action of the one resembled that of the other. With 1 mgrm. of free acid in 100 c.c. of distilled water the amount of oxygen taken up by the lead is markedly reduced. With smaller quantities, or with the same quantity of acid neutralised with sodium hydroxide or calcium hydroxide, the effect is very much less marked.

The acid present in the organic matter of moorland water may not be either citric or tartaric acid, but it is an acid acting in a similar manner upon metallic lead. The presence of such an acid explains why so many of the moorland waters examined deposited no oxycarbonate of lead, the water remaining perfectly bright when digested for 24 hours with lead-foil. In dealing with the pure neutral solutions of these salts very turbid liquids result which do not clear on standing for days, and the amount of lead in the poured-off or pipetted-off liquid varies very considerably, but in the presence of certain salts the liquid clears. The addition of a little barium chloride causes the precipitate to become flocculent, though it does not always clear the solution completely. This suggests that the colloid may be negatively charged. Sodium sulphate has no apparent effect.

ACTION OF HYDROXIDES.—Contrary to anticipation, it was found that the alkaline hydroxides had practically no effect in reducing the amount of lead oxidised, unless present in excessive quantities, but the amount of lead in solution, in suspension, and deposited on the foil varied to an extraordinary extent. With 2.5 per cent. of N/22 calcium hydroxide the liquid remained clear and bright, and a large proportion of the lead attacked remained in apparent solution, but some was deposited on the sides of the glass bottles, and the remainder was deposited on the lead-foil, which assumed a steel-like appearance. As the addition of lime water to certain natural waters prevents any solvent action taking place, it is

obvious that this is not due merely to the water being rendered alkaline, but to another cause which will be referred to in the next section.

That the mere acidity or alkalinity of a water is of minor importance is shown by the following results. A sample of distilled water of E.C. 2, and containing only about 0.1 part of carbon dioxide per 100,000, was employed, and minute quantities of other substances added to produce the requisite alkalinity or acidity.

	Substance added	Value of P_H	Appearance of liquid after acting on lead	Oxygen used Per Cent.	Amount of lead in drawn-off liquid Parts per 100,000
1	Lime water	9	Turbid	90	9.35
2	" " + silicic acid ..	9	Clear and bright	19	0.165
3	" " + citric acid ..	9	do	24	0.75
4	Sodium silicate + citric acid	4.5	Clear and bright	24	1.85
5	Citric acid only	4.5	Dull	76	2.05
6	Hydrochloric acid (N/22) ..	4.5	Dull	80	7.0

Obviously the P_H of any water affords no indication of the nature of its action on lead.

ACTION OF SILICIC ACID AND SILICATES.—A fresh solution of silicic acid was made by dialyzing a solution of sodium silicate acidified with hydrochloric acid. As this solution gelatinised in a few days, it had to be used in a fresh condition. The silicate used contained 35.15 per cent. of silicon dioxide and 22.7 per cent. of sodium oxide. A few of the results obtained are given in the subjoined table. The time of action was in all cases 24 hours.

	Silicic Acid				Sodium silicate expressed as Silicic Acid			
	0.75	1.0	1.5	2.5	0.3	0.6	0.75	1.0
In mgrms. per 100 c.c.	0.75	1.0	1.5	2.5	0.3	0.6	0.75	1.0
Oxygen used ..	0.95	0.94	0.95	0.37	0.87	0.325	0.130	0.15
= Lead oxidised ..	12.3	12.15	12.3	4.8	11.25	4.2	1.7	1.95
Appearance of liquid	Sheeny	Turbid	Turbid	Clear	Dull	Clear	Clear	Clear
Lead in liquid ..	5.5	3.25	1.0	0.05	5.75	0.02	0.02	0.01

Two extraordinary effects are brought out. First, that both silicic acid and silicates have a marked effect in retarding oxidation and in preventing lead passing into solution; and, second, that the alkaline silicate is several times more powerful than silicic acid. This explains why the neutralisation of certain acid waters by lime or soda reduces the plumbo-solvency so markedly. With solution of silicate in the purest distilled water, about 0.5 of silica is required to have a decided action, but in the presence of carbonates and sulphates a much smaller quantity is efficient.

ACTION OF VEGETABLE EXTRACTIVE MATTER.—Most of the moorland waters examined, and which will be referred to in the next and final section, contained from 1 to 4 parts of organic matter per 100,000; doubtless some markedly coloured waters contain more. This organic matter appeared to contain some salt of organic acids, as after burning off the carbon the soluble ash was alkaline to phenolphthalein, in some cases markedly so. This subject was briefly referred to under "citric acid." Many experiments were made with infusions of various kinds, and it was found that most of them, if used of sufficient strength, both retarded the oxidation of lead and reduced the plumbo-solvent action of the water.

An infusion of tea had the most pronounced effect, and with the idea that the tannin present might be the active principle, a number of experiments were made with tannin solutions; but it was soon obvious that this could not account for the action of moorland waters. Even with tea infusion, it was found that 13 mgrms. of the dried extractive had only an effect equal to 1 mgrm. of citric or tartaric acid.

Sphagnum, and Heather and Bilberry Plants.—A large number of experiments have been made with sphagnum, heather and bilberry plants and their products of decay, and all have been found to contain constituents soluble in cold water which have an acid reaction and contain acids and salts tending to retain lead in solution, but the subject must be left for later consideration. It suffices for the present to know that cold, exceedingly dilute, infusions of these plants possess the power of preventing the precipitation of lead by action of carbonates. That they also tend to retard the oxidation of the lead is of minor importance, since it is found that certain other constituents of moorland waters possess this power in a much higher degree.

Infusions of leaves and rootlets of bilberry and heather gave the best results, followed by infusion of sphagnum moss. With all these the effects produced could be imitated by using tartaric or citric acid, or possibly quinic acid, but only the two former in quantities likely to be present in moorland waters. The nature of the rocky surfaces and the kinds of plants growing upon them require investigation and relation to the character of the water draining therefrom. This has been done by Dachnowski for the State of Ohio, U.S.A., but unfortunately the analyses of the waters do not include the silica or state the nature of the organic matter. The association of a geologist, botanist, and chemist is required for the full investigation of this subject.

(To be continued.)

Notes.

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

LEAD IN SELF-RAISING FLOUR.

AN article of food largely used by children is pastry, frequently made from self-raising flour and baking powder. Ninety per cent. of the self-raising flour used in the United Kingdom contains, as the acid ingredient, acid calcium phosphate (or cream of tartar substitute).

Now the B.P. limits the lead in cream of tartar to 20 parts per million; yet acid calcium phosphate or cream of tartar substitute has no legal recognised

limit for *lead*. Recent tests have shown this substance to contain from 200 parts to 2000 parts per million of lead; yet it can be made as free from lead as tartaric acid and cream of tartar.

Acid calcium phosphate can be made with under 10 parts per million of lead, and is sold to-day with this guarantee by some firms.

N. T. Fox.

MANCHESTER.

THE TEMPERATURE COEFFICIENT OF THE REFRACTIVE INDEX OF AMERICAN TURPENTINE.

THE value given in Kanthack's *Refractive Indices of Essential Oils*, viz. 0.00037, is so low that it is quite outside the range for essential oils. A series of determinations at temperatures ranging from 14° to 60° C. has therefore been made upon four samples of the best varieties of American turpentine of normal composition, a recently-calibrated Pulfrich refractometer being used for the work. The refractive index (sodium flame) of the first sample was 1.47149 at 20.5° C.; 1.46272 at 39.2° C.; and 1.45420 at 57.4° C., and the mean temperature coefficient was 0.000468. Analogous results were obtained with the other three samples, which gave mean temperature coefficients of 0.000469 to 0.000470. There is little, if any, tendency for the temperature coefficients to alter with the temperature.

I wish to thank the Directors and the Chief Chemist (Mr. W. B. Parker, F.I.C.) of the British Thomson-Houston Co., Ltd., for permission to use the research laboratories for this purpose.

GARTHA THOMPSON.

HIGH STREET, RUGBY.

Sale of Food and Drugs Acts.

EXTRACTS FROM THE ANNUAL REPORT OF THE MINISTRY OF HEALTH FOR 1921—1922, AND ABSTRACTS OF REPORTS OF PUBLIC ANALYSTS FOR 1921.*

APPOINTMENT OF ANALYSTS.—The number of areas in England and Wales for which analysts are appointed is now 232. During the year the Department approved of 53 appointments in England.

PERCENTAGE OF ADULTERATION.—The total number of samples purchased for analysis under the Acts in 1921 was 113,664, of which 7582 (6.7 per cent.) were reported against. In 1920 the corresponding figures were 111,797 and 7903 (7.1 per cent.).

MILK.—Of the 61,439 samples purchased, 5290 (8.6 per cent.) were reported against, whilst in 1920 the percentage was 9.3 (5797 out of 62,463).

In London the proportion of adulterated milk was 5.1 per cent., as compared with 6.7 per cent. in 1920 and 7.7 per cent. in 1919. Of the 678 adulterated samples 357 contained extraneous water, 250 were deficient in fat, 33 were deficient in fat and also contained added water, 28 contained a colouring matter, 7 contained boric acid, 1 both boric acid and excess water, and 2 contained formaldehyde.

In the 40 largest provincial towns in England and Wales the proportion of

* H.M. Stationery Office, 1922. Price 1s. 6d. net.

adulterated milk samples was 9·6 per cent., and in the remainder of the country, excluding London, it was also 9·6 per cent. Of the total milk samples in the whole country 114 contained a colouring matter, in most cases annatto.

CREAM.—Of the 984 samples of ordinary cream, 315 contained preservative, and 86 of the 707 samples of preserved cream contained preservative in excess of the permitted amount or otherwise contravened the Regulations. No preservative other than boric acid was found.

BUTTER AND MARGARINE.—In 1921 Public Analysts reported against 245 out of 10,236 samples of butter (2·4 per cent. as compared with 3·6 per cent. in 1920). Of these adulterated samples 129 contained foreign fat, in the majority of cases in large proportions; 2 contained foreign fat and excess of water, 96 contained excess of water only; 7 an excessive amount of preservative and water; and 2 were rancid.

Of the 4296 samples of margarine submitted, 31 were reported against, 21 for excess of water, 6 for excessive preservative, 3 for the presence of more than 10 per cent. of butter fat, and 1 on account of rancidity.

CHEESE.—Forty-seven out of 1178 samples were reported against, mostly for high percentages of water. Four samples contained large amounts of foreign fat.

EDIBLE FATS AND OILS.—During the year 3490 samples of lard were examined, of which 5 were found not genuine; 692 samples of dripping and cooking fats, of which 41 were adulterated. The adulterations consisted of excess of water or free fatty acids, the addition of foreign fats, and in the case of suet, undeclared flour and starches. Six of 432 samples of olive oil were condemned on account of the presence of other oils, such as cottonseed or arachis.

COFFEE AND COCOA.—The number of samples purchased was 2191, of which 32 were adulterated with chicory. Of the 1382 samples of cocoa submitted, only 7 were reported against, 4 being greatly deficient in cacao butter, 2 containing sugar, and 1 both sugar and arrowroot.

FLOUR AND BAKING POWDER.—Of the 507 samples of ordinary flour only 17 were condemned, 16 containing a persulphate improver, and one consisting of self-raising flour. Seven of the 806 samples of self-raising flour were condemned, most of them containing slight excesses of calcium sulphate.

MISCELLANEOUS ARTICLES OF FOOD.—Three of 947 samples of sugar were condemned. Of 168 samples of preserved peas taken, 73 were reported against on account of containing copper salts. The vendor of spinach containing 6·8 grains of copper per lb. was fined £20.

A concentrated fruit syrup was reported upon by the Public Analyst for Durham as being in no sense a "fruit syrup," since it was free from any trace of vegetable colouring matter or of any organic acid naturally found in fruit. It consisted of a solution of sugar coloured with a coal tar dye and acidulated with phosphoric acid. The vendor was fined £5.

In Surrey large fines have been inflicted under the Sale of Food and Drugs Acts and the Merchandise Marks Acts for the sale of "lemon squash" and "lemonade" consisting of effervescing solutions of sugar flavoured and acidified with phosphoric acid.

DRUGS.—Of the 5589 samples examined, 374 (6·7 per cent.) were found not genuine. In all 123 different kinds were selected for analysis, and 42 of them yielded adulterated samples. The principal drugs examined and the numbers of samples condemned were as follows:—Borax, 214 (43); camphorated oil, 490 (45); cream-of-tartar, 453 (18); magnesia and preparations of magnesia, 109 (26); mercurial ointment, 110 (21); Gregory powders, 153 (24); and sweet spirits of nitre, 85 (20).

Report of the Government Chemist

UPON THE WORK OF THE GOVERNMENT LABORATORY

FOR THE YEAR ENDING MARCH 31, 1922.*

THE total number of samples examined was 302,562, as compared with 308,675 in the preceding year, the decrease having been in the samples examined at the chemical stations, whilst the number examined at the central laboratories showed an increase of 5687.

The most notable addition to the work of the department has been in connection with the Safeguarding of Industries Act, 3000 samples having been submitted in the six months October to March.

ADMIRALTY.—The total number of samples examined was 690, and included ferrous and non-ferrous metals, fuel oils, rubber washers and valves, fabrics for sail cloths, and paints, in addition to food samples from the victualling yards.

MINISTRY OF AGRICULTURE AND FISHERIES.—(1) *Imported Dairy Produce and Margarine.*—Of the 465 samples of butter examined 8 contained more than 16 per cent. of water, and 2 were adulterated with animal fat. Six samples of margarine out of 712 contained excess of water; there was no excess of butter in any of them.

Cheese.—All of the 121 samples examined were satisfactorily marked. Incidentally, the proportion of fat was found to vary from 9·9 to 38·8 per cent.

Cream.—Thirteen samples of tinned sterilised cream were examined. They contained 21 to 29 per cent. of fat and were free from preservatives.

Condensed Milk.—Five of the 469 samples examined had been prepared from skimmed milk, but there were no marks on the packages to indicate the removal of fat. The amounts of fat in the remainder of the samples varied from 7·15 to 10·6 per cent., with a corresponding range in the non-fatty solids. No exception could be taken to the milk with the low proportion of fat, as minimum limits for condensed milk have not yet been adopted in this country.

(2) *Butter and Margarine Samples taken at Factories in this Country.*—Fourteen of the 172 samples taken at butter factories in Ireland contained over 16 per cent. of water.

(3) *Sheep Dips.*—Dips must be prepared in accordance with a formula approved by the Ministry, and the bath prepared from it must be of approved strength. Of 158 samples submitted 53 were reported as defective.

(4) *Water and Pollution of Rivers.*—During the year 92 samples of river water and effluents were examined. Steps are being taken to ascertain the condition of fishing streams from the point of view of fish life and the effect of certain types of pollution on fish and fish food. An interim report on the examination of road drainage and tars was issued by the Ministries concerned (Paper No. 149, Roads, March, 1922).

(5) *Sea Water.*—The salinity of 5011 samples was determined, and experiments have been made to discover a method capable of ready application at sea.

(6) *Fertilisers and Feeding Stuffs Act.*—During the year 17 fertilisers and 8 feeding stuffs have been reported upon. The fertilisers consisted of super-phosphate, basic slag, compound fish guano, top-dressing fertiliser and compound manure. In most cases the amounts of nitrogen, phosphates or potash were less than the guarantee stated. A sample described as compound fish guano afforded

* H.M. Stationery Office, 1922. Price 1s. 6d. net.

no evidence of fish. In some of the feeding stuffs there was a deficiency in oil or albuminoids compared with the guarantee on the invoice, but one sample contained more of both substances than the guarantee, and the invoice was therefore not in accordance with the requirements of the Act.

In all cases there was substantial agreement with the reports of the agricultural analysts who had first examined the samples.

A sample of "thirds" or milling by-product was found to contain nearly 70 per cent. of ground vegetable ivory; a barley and wheat meal contained over 10 per cent. of chalk; and a sample of sharps was adulterated with 40 per cent. of oat husks and 5 per cent. of bean meal.

(7) *Merchandise Marks Act.*—Several samples of feeding stuffs were examined in connection with proceedings under this Act. In one case pea or bean flour had been supplied in place of millers' flour sweepings. Another sample, purporting to be biscuit meal, consisted of sour, mouldy lumps of biscuit damaged by fire and water, mixed with cement, plaster, burnt wood, paper, coarse string, and glass. A sample of oat feed contained 53 per cent. of gypsum.

(8) *Miscellaneous Articles.*—These consisted of materials suggested as of value for fertilising purposes or as cattle food. The Ministry submitted 185 samples. Seventy samples were examined with reference to the quality of blue vitriol supplied for horticultural and wheat-dressing purposes throughout the country. Of these, 55 contained more than 98 per cent. of crystallised copper sulphate, and 7 were almost up to this standard. Two samples, however, were mixtures of copper sulphate with about 50 per cent. of ferrous sulphate. A number of dead bees were examined, but no evidence was obtained of either arsenic or lead, which, it was suggested, might have been derived from insecticides on plants.

AIR MINISTRY.—Samples (222) of various metals and alloys used in aircraft construction were examined.

CUSTOMS AND EXCISE.—As a check on the work of the officers at the chemical stations the residues from 1277 samples were re-tested at the Government laboratory. The results indicated that the testing work at the stations is very efficient.

BEER.—The total number of samples examined was 29,642, being an increase of about 1500. There were also examined 265 samples of materials used in brewing, and 8503 samples of worts or unfinished beer, as a check on the assessment of beer duty. The original gravity of the worts was declared by the brewers at a figure between one and five degrees less than the true gravity in 2902 cases, and exceeding five degrees in one case.

The number of samples of sour and unsaleable beer submitted, to obtain remission of the duty, was 1923, being an increase of 629 on last year's number, and of 1153 on that of the previous year.

Beer as Retailed.—In 211 instances out of 4650 samples examined there was evidence of dilution, and in 26 cases the dilution was equivalent to over 4 gallons of water per barrel.

Non-Alcoholic Beers.—In 8 of 139 samples examined the proof spirit was between 2 and 5 per cent., and in one instance it exceeded 5 per cent. Of the remaining 113 samples (herb beers, ginger beers, etc.), 48 contained between 2 and 5 per cent. of proof spirit, and one contained over 8 per cent.

Beer Exported on Drawback.—The number of cases of over-declaration was 79, and was small compared with the number of check samples, viz. 13,599. It may be mentioned that lager beer is now being brewed in this country, and that a certain proportion of it is being exported.

Imported Beer.—The quantity is still insignificant compared with that of pre-war times. Last year only 700 samples were examined, as against 10,000 in the year ending March, 1914.

Examination of Beer and Brewing Materials for Arsenic.—Twenty-four of the 481 samples contained arsenic in excess of the limits fixed by the Royal Commission on Arsenical Poisoning.

COCOA AND CHOCOLATE.—During the year 7266 samples were examined to ascertain the relative amount of raw cocoa for duty purposes. The method of detecting and estimating foreign fat in chocolate (ANALYST, 1921, 46, 229), has continued to give satisfactory results. Of the samples of chocolate confectionery examined 1797 contained spirit, in many cases derived from the flavouring essence used. Most of these fell within the section of the tariff providing for the imposition of an additional duty of $\frac{1}{4}$ d. or 1d. per lb.

Dangerous Drugs Act.—Eighty-seven suspected samples were forwarded by the Officers of Customs and Excise, and of these 14 contravened the provisions of the Act.

Matches.—None of the 86 samples examined showed any evidence of the presence of white phosphorus.

Safeguarding of Industries Act.—Over 3000 samples were received, and in many cases special methods of analysis had to be devised for their examination.

Spirits.—The naphtha represented by 689 samples out of 694 examined was approved as fit for methylating purposes. An enquiry has been carried out into the characteristics of denaturants for industrial alcohol.

Exported Spirits.—The number of samples of gin, cherry brandy, etc., tested to check the exporters' claim for drawback was 1805. The strength of spirit or quantity of sugar was overstated in 231 cases. During the year 13,247 samples of tinctures, medicinal spirits, etc., were also examined.

Fusel Oil.—Forty-six samples from British distilleries were examined, and of these 14 contained more than 15 per cent. of proof spirit. Eleven of the 85 samples of imported fusel oil also contained excess of spirit.

Imported Spirits.—The number of samples was 10,790, a decrease of 5894 on last year's number.

Sugar, Glucose and Saccharin.—The number of samples containing sugar or other sweetening matter examined for assessment of duty was 42,715, as compared with 32,332 last year; 149 samples of imported substances were tested for saccharin.

British Sugar Manufacture.—In connection with the production of sugar from home-grown beet 132 samples of refined sugar, molasses, beet juice and beet pulp were examined.

Tea.—The total number of samples examined was 42,047, and of these 5243 were reported against, mainly on account of foreign substances, which could not be attributed to intentional adulteration; 1564 were condemned as unfit for human consumption. The number of samples examined with a view to denaturation and extraction of caffeine was 668.

Tobacco.—The moisture was estimated in 284 samples of unmanufactured tobacco, and 7 were submitted for decision whether the tobacco was liable to duty as "leaf" or "strip." Seventeen of 46 samples of imported tobacco and snuff contained prohibited ingredients. Seventy-four samples of leaf tobacco experimentally grown in Ireland, East Anglia and the south of England, were examined. The percentage of moisture was estimated in 10,913 samples of manufactured tobacco, and the percentage of oil in 1519 samples from the stocks of 212 manufacturers and retailers. One hundred and forty-nine samples of materials were approved as denaturants, and 108 samples of nicotine preparations, of the 110 examined, were approved for delivery free of duty. Four samples of preservatives containing either sugar, sulphuric acid or benzoic acid derivatives could not be approved, as acetic acid is the only legal preservative.

Wines.—The total number of samples examined was 61,683, being a decrease of 9476 on last year's number.

DISPOSAL BOARD.—Upwards of 300 mgrms. of radium bromide of over 90 per cent. purity were recovered from one batch of luminous dials, gunsights, etc., and, in addition, some 100 mgrms. of highly concentrated material were recovered in a state suitable for immediate use.

HOME OFFICE.—Investigation of lead glazes has been continued, and an enquiry has been made as to the quantity of lead, derived from the paint, rising as fume from the hot metal during the cutting of the steel plates of old ships by means of oxy-acetylene burners. (*Cf. Annual Report of Chief Inspector of Factories for 1921, p. 69.*)

Specimens of dust in the exit tube of a plant used in bleaching flour contained large amounts of basic tin nitrate. This substance may decompose with violence under certain conditions, and it was the cause of an explosion which occurred during the repair of the plant.

POST OFFICE.—The paper, pigments and gum used in the manufacture of stamps were systematically examined for quality and freedom from deleterious substances. Other samples examined included postal obliterating fluids, creosote oils, copper sulphate and miscellaneous stores. Samples of air were examined for the Medical Department.

BOARD OF TRADE.—The quantity of lime juice approved was 21,342 gallons. Fifty-six samples of foods for ships' stores were also examined.

WAR OFFICE.—The number of food samples examined was 1470, and five samples of anæsthetics and drugs were analysed.

OFFICE OF WORKS.—The samples examined consisted largely of materials purchased for the public service. Special analyses were also made of paint that had been exposed to the London atmosphere for some years. Several stone "preservatives" were examined, but nothing better than the older preparations was discovered. Treatment of existing decaying structures can only afford limited protection, and in certain cases may increase the damage, by the production of hard surfaces which break away in flakes.

SALE OF FOOD AND DRUGS ACTS.—Seventy samples were examined during the year, including 59 milks, 5 butters, 2 calcined magnesias, a cinnamon, a rum, a bloater paste, and an olive oil. In 57 cases the results were in agreement and in 8 cases in disagreement with those put forward by the prosecution. Certificates were not issued in the case of two milks which were in an advanced stage of butyric fermentation, and in three cases a comparison between the laboratory and the prosecution results could not be made. Four milks alleged to be deficient in fat were found to contain 3.25, 3.34, 3.60, and 6.07 per cent. respectively of fat. Of 2 milks alleged to contain less than 8.5 per cent. of non-fatty solids 8.51 per cent. of non-fatty solids was found in one, and the other contained 8.46 per cent. of non-fatty solids at the time of the examination, without taking into account the loss during fermentation. In one sample alleged to contain added water, the percentage of non-fatty solids was abnormally high, but in this case there was some evidence that the results had been affected by leakage from the bottle, although the seal was intact.

A sample of olive oil alleged to contain arachis oil afforded no evidence of that oil, and a butter, the charge against which was that it was composed almost entirely of margarine, gave the following results:—Reichert-Wolff value, 27.75; Polenske value, 2.0; and Kirschner value, 23.4; which showed that no margarine was present.

STAFF.—The technical staff of the Department consists of: The Government Chemist, Deputy Government Chemist, 5 Superintending Chemists, 9 Chemists (Class I.), 23 Chemists (Class II.), and 36 Temporary Assistant Chemists. During the year the permanent staff was increased by three chemists (Class II.), and the staff of Temporary Assistant Chemists reduced by six.

Legal Notes.

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

DEFINITION OF COD OIL.

IN the case of *Bowring and Co. v. Kendall*, tried in the Chancery Division on July 14, 1922, the plaintiffs sought an injunction to restrain the defendant from being engaged in the business of fish or whale oil extractor, refiner or manufacturer, within 100 miles of Grimsby, for a period of fifteen years from August, 1917. On that date the plaintiffs had purchased the business from the defendant, and had obtained from him a covenant, in the terms mentioned, not to compete with the business so purchased.

For the defence it was argued that fish oil was a low-grade oil made from the bodies of small fish, such as the herring and the menhaden, and that the covenant entered into by the defendant did not prevent him engaging in the manufacture of cod oil or oil made exclusively from the livers of cod, or cod and other large fish.

Mr. Justice P. O. Lawrence, giving judgment, accepted the text-book classification of marine animal oils into (a) fish oils, (b) liver oils, and (c) blubber oils, in which classification fish oils were confined to oil extracted from the whole bodies of fish. But it would be wrong, he considered, to apply that definition to the case in question. The defendant had established a cod oil business in 1910. During the war livers were difficult to obtain, and oil was extracted from fish bodies and blubbers, but whenever the defendant could obtain livers he did so, and the plaintiffs' object in buying was to carry on a cod oil business. Under these circumstances it was difficult to imagine that they would be at pains to prevent the defendant carrying on a business which he had only spasmodically engaged in when the war interrupted the main business, and at the same time leave the defendant free to carry on the main business in competition with the undertaking they were buying.

It had been argued that the inclusion of whale oil in the covenant narrowed the meaning to be given to the expression "fish oil," because whale oil was sometimes sold as fish oil. In this agreement, however, it seemed that the parties were distinguishing between oil extracted from fish and oil extracted from marine animals other than fish. The words had to be considered in their natural and ordinary signification. Accordingly he granted the injunction sought by the plaintiffs.

ALLEGED EVAPORATION OF WHISKEY.

ON September 6, 1922, the licensee of a publichouse was summoned at Leeds for selling whiskey containing 3 per cent. more water than the permissible maximum.

For the defence it was urged that the loss was entirely due to evaporation. The whiskey was drawn through pipes from a cask which would hold 28 gallons,

and there were always about two gallons of whiskey left in the cask below the level of the pipe. When, as occasion required, a few gallons at a time were added, there was always a big space left in the cask, which caused evaporation.

A witness for the defence, who stated that he had had a life-long experience in the trade, said that the air space in the cask would be likely to cause evaporation. When, as in this case, about eight gallons of whiskey were poured into the cask, they would not mix properly with the old spirit at the bottom unless properly "roused." It was well known that evaporation took place, and the average bonded warehouse lost about 2 per cent. of the spirit per annum. The witness agreed that the best plan would have been for the defendant to have obtained a smaller barrel, so that there would not have been so much air space.

The Stipendiary Magistrate said that he accepted the explanation, though something would have to be done on the lines suggested. He adjourned the case for six months, and the defendant would have to pay the costs, if there were no complaint in the meantime. There would not, he said, be a conviction if all was well.

Ministry of Health.

THE following correspondence relates to Circular 325 (ANALYST, 1922, 397):

THE SECRETARY,
MINISTRY OF HEALTH,
WHITEHALL, S.W.1.

August 28th, 1922.

SIR,—The attention of the Councils of the Institute of Chemistry and of the Society of Public Analysts has been directed to a copy of a circular purporting to have been issued by the Ministry on 17th July, 1922, with regard to taking proceedings against milk vendors who sell milk containing less than the proper amount of fat.

In this circular it is stated that the Ministry is of opinion that it is extremely undesirable that a prosecution should be based upon the results of an isolated test when other tests of the particular milk supply have proved satisfactory, and that in such cases prosecutions should be instituted only where a series of tests have shown repeated default.

The Councils of the Institute and the Society feel that the instances in which the fat content of milk falls below the fixed limit are so rare and unusual that the action of the Ministry in the issue of this circular constitutes a dangerous menace to the public health in the administration of the Act. Already cases have been reported to the Councils wherein the local authorities have acted upon the circular and cases of undoubted adulteration have thus escaped any form of penalty.

The Councils hope, therefore, that the Ministry will see their way to withdraw or modify the circular referred to.

Yours faithfully,

(Signed) A. CHASTON CHAPMAN
(President of the Institute of Chemistry).

P. A. ELLIS RICHARDS
(President of the Society of Public Analysts).

The following reply was sent to the Presidents of the two Societies:—

[COPY.]

MINISTRY OF HEALTH,
WHITEHALL, S.W.1.

11th September, 1922.

161069/22.

CIRCULAR 325.

SIR,—In reply to your letter of the 28th ultimo, I am directed by the Minister of Health to state that he is aware of the considerations put forward by the Institute of Chemistry and the Society of Public Analysts as to the difficulty of obtaining convictions against milk vendors for adulterating milk. It appears to him, however, that there is considerable misapprehension as to the precise purport and scope of the Circular issued on the 17th July last.

I am to point out that the advice given in the Circular is limited to those cases in which a milk vendor has held a good record for a number of years and in which, during that period, constant tests of his milk have given uniformly satisfactory results. It is only in such cases that the Circular deprecates the institution of a prosecution based upon the results of an isolated test.

I am, Sir, your obedient Servant,

(Signed) H. A. DE MONTMORENCY
(Secretary to the Ministry).

[The Hon. Secretary of the Society would be glad to have particulars of further cases in which proceedings have not been instituted as a result of this Circular.]

SALICYLIC ACID IN COFFEE ESSENCES.

DR. HOWARTH, Medical Officer of Health for the City of London, has called the attention of the Corporation to the presence of salicylic acid in coffee and chicory extracts. The Corporation has adopted his suggestion that after January 1st, 1923, the addition of salicylic acid will be regarded as an adulteration, and proceedings will be taken when such adulteration is detected.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Wheat Gluten. J. Gerum and C. Weizenkleber. (*Zeitsch. Unters. Nahr. Genussm.*, 1922, 44, 86–89.)—It is shown that in the separation of gluten by washing the dough in a stream of water the compound formed by the albumin and phosphorus is partly decomposed, much of the phosphoric acid passing into the wash-water. Wheat meals examined were found to contain from 0.151 to 0.319 per cent. of phosphoric anhydride, and yielded from 26.8 to 30.8 per cent. of dry gluten containing 0.0308 to 0.0719 per cent. of phosphoric anhydride; which shows that the gluten only retains from 17 to 22.5 per cent. of the total phosphoric acid in the meal. There does not, however, appear to be any quantitative relationship between the total amount of phosphoric acid in the meal and that retained by the gluten. The admixture of rye flour with wheat meal reduces the amount of phosphoric acid retained by the gluten separated from it, 30 per cent. of rye flour reducing the percentage retained by the gluten by one half. H. E. C.

Composition of Taamya (an Egyptian Food). A. Azadian. (*Ann. Falsific.*, 1922, 15, 278-282.)—Taamya is prepared by grinding the beans of a plant (family, *Papilionaceæ*) grown extensively in Egypt, mixing the flour with water, spices, etc., cutting up the dough into small pieces and frying these in hot sesame oil or cottonseed oil. If desired, the beans are moistened and allowed to germinate for twenty-four hours previous to grinding. The product has the following composition: Moisture, 22 to 33; proteins, 14.2 to 16.2; fat, 20.0 to 31.6; ash, 3.4 to 7.1; cellulose and starch, 18.0 to 29.3 per cent. W. P. S.

Adulterated Chestnut Product. Gabriel. (*Ann. Falsific.*, 1922, 15, 267-289.)—A product sold as chestnut *puree* was found to contain a foreign substance which microscopical examination showed to be sweet potato flour; the latter is characterised by the large number of calcium oxalate crystals present in the cells and by groups of elongated pitted cells. W. P. S.

Tea Containing Lead. F. Wirthle and K. Amberger. (*Zeitsch. Unters. Nahr. Genussm.*, 1922, 44, 89-91.)—A case is recorded in which a consignment of tea was seriously contaminated with lead on account of prolonged storage in tea chests lined with foil which had become brittle. The tea contained numerous tiny metallic particles which proved to be foil (containing 84.4 per cent. of lead); the amount present in the tea was estimated as from 2.19 to 4.53 per cent. in various samples. In order to decide whether this would be injurious to health, experiments were made by macerating for five minutes with 200 c.c. of hot distilled water and tap water respectively, 1.5 gm. of pure tea to which had been added 0.0328 and 0.068 gm. of lead-foil. After straining off the tea leaves the following results were obtained:

		200 c.c. of liquor contained:—	
		Lead in suspension	Dissolved lead
Distilled Water	0.0328 foil	1.85 mgrm.	1.6 mgrm.
	0.0680 foil	3.82	3.4
Tap Water	0.0328 foil	3.6 mgrm.	1.1 mgrm.
	0.0680 foil	5.7	1.0

A cup of the tea (say 200 c.c.) might contain from 1 to 3.4 mgrms. of lead, which amount must be considered as prejudicial to health, in view of the quantities of tea commonly consumed. H. E. C.

Estimation of Sucrose in the Presence of other Carbohydrates by means of Alkaline Earth Hydroxides. A. Behre and A. Düring. (*Zeitsch. Unters. Nahr. Genussm.*, 1922, 44, 65-70.)—When a solution containing sugars is boiled with an alkali metal hydroxide all the sugars commonly occurring in foodstuffs are decomposed except sucrose, but certain secondary products are liable to be formed which may introduce errors in the estimation. When an alkaline earth hydroxide is substituted for that of sodium or potassium the decomposition proceeds more slowly, and there are no troublesome by-products;

one hour's heating at from 60° to 80° C. with lime, or two hours' boiling with baryta, is sufficient to decompose all the sugars except sucrose. The procedure is to heat 10 grms. of the mixed sugars with 40 c.c. of water and 0.6 gm. of freshly-ignited calcium oxide in a 100 c.c. flask for an hour at from 60° to 80° C., to cool, neutralise at 15° C. with mineral acid, make up to the mark and determine the optical rotation at 20° C. The method is well suited for the estimation of sucrose in honey and mixtures with invert sugar. The solution, after warming, darkens in colour, but, after neutralisation and dilution, it is usually possible to make a good reading on the polarimeter; lead acetate and sodium phosphate may be used for clearing purposes, if necessary. The polarimetric observation should be made as soon as possible after neutralisation and exactly at 20° C., as a small error in the temperature reading introduces a large error in the result; excess of acid in neutralising should be avoided. For the estimation of sucrose in admixture with lactose in chocolate and milk products, the sample is dissolved in 50 c.c. of water, 1.2 gm. of lime added, and the solution made up to 70 c.c. and heated as before, after which it is neutralised with 1.4 sulphuric acid, then treated with 5 c.c. of lead acetate solution and 1 c.c. of sodium phosphate, made up to 100 c.c. and filtered, and the rotation of the filtrate observed in a 200 mm. tube. Using a Laurent half-shadow polarimeter and starting with 50 c.c. of a 20 per cent. solution of the material, the sucrose content is given by the equation $x = P \times 0.75 \times 5$, where P is the observed polarimeter reading.

H. E. C.

Inversion of Sucrose by Alkaline Copper Solutions. M. L. Maquenne. (*Bull. Soc. Chim.*, 1922, 31, 799-806.)—When pure sucrose is heated with alkaline copper solutions it is partially inverted, the amount of invert sugar produced depending upon the concentration and volume of the sucrose solution and the temperature and duration of heating. To avoid errors due to this source in the estimation of invert sugar, the author prepares solutions for gravimetric Fehling estimations by adjusting the weight of material under examination and, if necessary, by the addition of pure sucrose to give a constant concentration of this sugar. Two standardised methods are adopted: In the first a volume of solution containing, in addition to invert sugar, 10 grms. of sucrose, is added to 20 c.c. of mixed Fehling solution to give a total volume of 36.2 c.c., and the solution is heated to boiling for 3 minutes, or, alternatively, the solution containing 20 grms. of sucrose is made up to a final volume of 42.5 c.c., and is heated at 65° C. for 10 minutes. After reduction in each method, potassium iodide is added, and the liberated iodine is titrated with standard sodium thiosulphate solution. Concordant results are obtained with the two methods when allowance is made for the invert sugar derived from the sucrose, and the accuracy obtainable is approximately 0.005 per cent. of the sugar examined. The titration with sodium thiosulphate is inapplicable to the examination of molasses and distillery worts owing to the presence of substances which absorb iodine, but accurate results may be obtained with these materials by the Bertrand permanganate method. Details of several experiments and three tables showing the relation between the sodium thiosulphate solution used and the invert sugar present are given.

T. J. W.

Elderberry Wine. J. Prescher and R. Claus. (*Zeitsch. Unters. Nahr. Genussm.*, 1922, 44, 92-93.)—The suggestion that elderberry wine prepared from the black berries of *Sambucus niger* contains poisonous substances produced during its fermentation is disproved. Wine produced by boiling 25 litres of the berries with 15 litres of water in nickel pans, with subsequent filtration, pressing and sweetening ($\frac{1}{2}$ lb. of sugar to 1 litre of juice) was fermented in wooden vats for three days, then stored in loosely-bunged casks for several months; when examined it had the following chemical characteristics: Sp. gr. 1.025; optical rotation in 1:10 dilution in 200 mm. tube, -0.50° ; alcohol, 9.78 grms. per 100 c.c.; extract, 7.91; invert sugar, 1.35; total acid (as tartaric acid), 0.73; volatile acid (as acetic), 0.200; and mineral matter 0.416 per cent. It yielded no hydrocyanic acid on hydrolysis or distillation, and the supposed formation of hydrocyanic acid by the action of the gastric juice on the glucosides of the elderberry was negated by experiments. The nausea and vomiting which have sometimes been observed after the taking of this wine may possibly be due to metallic poisons, such as might be introduced by the use of zinc vats during the fermentation process.

H. E. C.

Estimation of the Volatile Acidity of Wines containing Sulphurous Acid. R. Marcille. (*Ann. Falsific.*, 1922, 15, 269-274.)—When a solution containing sulphurous acid is oxidised with iodine, the original acidity of the solution is doubled: $\text{SO}_2 + 2\text{H}_2\text{O} + \text{I}_2 = \text{H}_2\text{SO}_4 + 2\text{HI}$ —or, in other words, the increase in acidity corresponds with the amount of free sulphurous acid present. In the case of wines a part of the sulphurous acid is combined with aldehydic substances, etc., and is not oxidised by iodine. Based on these facts, the following correction is proposed for determining the volatile acidity of wine. From the total volatile acidity is subtracted a quantity equal to the sum of the sulphurous acid oxidisable by iodine and 70 per cent. of the combined sulphurous acid. The amount of combined sulphurous acid is found by subtracting the amount oxidisable by iodine from the total sulphurous acid.

W. P. S.

Absorption of Water by Hardened Fats. K. Brauer. (*Chem. Zeit.*, 1922, 46, 793-794.)—When hardened fat prepared from whale oil was melted, pounded with water, and then subjected to high pressure, its water-content was 23.1 per cent. This is much higher than the values obtained with other hardened fats or with untreated fats, and if hardened whale oil is used for making margarine, care must be taken lest the latter contain more than the permissible proportion of water.

T. H. P.

Detection of Iodates in Potassium Iodide. M. Lachartre. (*J. Pharm. Chim.*, 1922, 26, 134-138.)—The French Codex (1908) lays down that a solution of potassium iodide in recently-boiled distilled water, when acidified with acetic acid and shaken with carbon disulphide or chloroform, should not give a violet coloration, but it is necessary to define the conditions of the test more accurately. The strength of the solution, the quantity and dilution of the acid, and the length

of time of observation all play a part. In order to find the minimum quantity of potassium iodate corresponding to a positive reaction, in terms of the Codex, a series of test tubes was prepared, each containing 10 c.c. of 10 per cent. potassium iodide solution, and potassium iodate in quantities ranging from 0.00001 to 0.0001 grm. To each tube 3 c.c. of chloroform and 5 drops of glacial acetic acid were added, and after vigorous agitation, the chloroform appeared distinctly coloured in the tube containing 0.00008 grm., the Codex reaction thus being sensitive to 0.08 grm. per 1000. This result is, however, only comparative, depending entirely on the experimental conditions, and the time factor is important, as air and light have a distinct action on the potassium iodide solution. The presence of small quantities of copper in the distilled water has no effect on a pure iodide, but causes a notable quickening of the development of the yellow colour given by iodides containing traces of iodates. The U.S. Pharmacopœia reaction is sensitive to 0.0005 part of iodate, and the German Pharmacopœia test will detect 0.0004 part per thousand.

D. G. H.

Estimation of Sulphate in Neo-arsphenamine. E. Elvove. (*J. Ind. Eng. Chem.*, 1922, 14, 624-625.)—A method is described for the estimation of sulphate in neo-arsphenamine (3.3-diamino-4.4-dihydroxyarsenobenzene-N-methylenesulphonic acid) without preliminary precipitation, filtration, etc., of the formaldehyde-sulphoxylic acid derivative of the arseno base, as required in a method described previously by Raiziss and Falkov. The latter method, however, yields higher results, probably owing to oxidation of sulphur during the operations. The details of the direct method are as follows:—Two hundred c.c. of water are boiled until the volume is reduced to about 150 c.c., and 0.2 grm. of the sample is then added and dissolved by stirring. Ten c.c. of *N* hydrochloric acid are added, and the liquid is boiled until the volume is reduced to about 50 c.c. The solution is diluted with water to 150 c.c., boiled, and treated with barium chloride solution. The precipitated barium sulphate is collected, ignited and weighed. The quantity of sulphate, calculated as anhydrous sodium sulphate, found in thirty-four samples of the substance from ten manufacturers varied from 1.4 to 17.6 per cent., although there was but little variation in the amounts present in the samples from each individual maker.

W. P. S.

Identification of the Colouring matter of Saffron. M. Guerbet. (*J. Pharm. Chim.*, 1922, 26, 218-220.)—Weiss has shown that with concentrated sulphuric acid, crocein, the colouring matter of saffron, gives an indigo-blue colour passing to violet and then to brown, but that the reaction is very much more definite if the condensation product, crocetin, is used. In contradistinction to crocein, crocetin (a red powder) is insoluble in water and dilute acids, and easy to isolate and detect in substances coloured with saffron. *Use of the Reaction in the Investigation of cases of Laudanum Poisoning.*—One c.c. of Sydenham's laudanum (a compound tincture of opium containing saffron) is treated with 5 c.c. of 10 per cent. hydrochloric acid, and the mixture boiled under a reflux condenser for

15 minutes. The crocetin is deposited, on cooling, as a brown precipitate; it is separated and washed on the filter paper with a few drops of water. The paper is dried, and, on dissolving a particle of crocetin in a drop of concentrated sulphuric acid, an intense indigo-blue colour is immediately produced, changing in a few seconds to violet and then to brown. With smaller quantities the reaction may be carried out on the filter paper. This reaction allows of the easy detection of meconic acid and opium alkaloids in the acid liquid from which the crocetin has been removed.

D. G. H.

[Saffron was a constituent of *Tinctura opii ammoniata* in the B.P. of 1885, but is no longer an official drug in this country.—EDITOR.]

Volatilisation and Hydrolysis of Atropine in Toxicological Investigations. P. Hardy. (*J. Pharm. Chim.*, 1922, 26, 220–226.)—Chemists agree that in the estimation of atropine and hyoscyamine in viscera by the Stas method, which is that usually adopted, there are many difficulties owing to loss of alkaloid, and a detailed study of the conditions involved was therefore made. The volatility of atropine was studied both in the dry condition and in ethereal, alcoholic and chloroform solutions, and in water vapour; whilst its hydrolysis was investigated in solution in water, alcohol, and tartaric acid solutions and in alkaline sodium and ammoniacal solutions; and the following conclusions were arrived at: (1) There is no loss of atropine by volatilisation in toxicological extractions. (2) The hydrolysis of atropine is sensibly increased with a rise in temperature, and is greater in alkaline sodium solutions than in ammoniacal solutions, in which it proceeds as in aqueous solution at ordinary temperature; and to these facts must be imputed the loss during estimation. By adopting Osier's modification of the Stas method, which prevents emulsions between the alkaline alkaloidal solution and the extracting liquid by eliminating albuminoid and gummy matter by precipitation with alcohol, the loss may be greatly diminished, if not entirely eliminated.

D. G. H.

Preparation and Analysis of Animal Nucleic Acid. P. A. Levene. (*J. Biol. Chem.*, 1922, 53, 441–447.)—The following method is a modification of one previously devised by the author, but found to give unsatisfactory results when adopted by other workers. Five kilos. of the glandular organ, such as thymus gland, spleen, liver, etc., are freed from fat by dissection, finely minced and stirred into 5 litres of 5 per cent. sodium hydroxide solution. The mixture is boiled for thirty-five minutes and neutralised with acetic acid, after which 50 c.c. of colloidal dialysed iron solution containing 5 per cent. of ferric oxide are added, and the solution is filtered and allowed to stand overnight. The liquid is treated with twice its volume of methyl alcohol containing 2 per cent. of hydrochloric acid, and the resulting precipitate filtered off and washed with methyl alcohol until free from acid. The precipitate is purified by dissolving it in water containing a minimum amount of alkali, slightly acidifying the solution with hydrochloric acid, and precipitating the nucleic acid by the addition of 20 per cent. cupric chloride solution. The precipitate is washed with water, suspended in alcohol containing 2 per cent. of hydrochloric acid and carefully broken down until most of the copper is

removed, after which it is again dissolved in water containing a minimum quantity of alkali, and the pure nucleic acid is precipitated by the addition of twice the volume of alcohol containing 2 per cent. of hydrochloric acid. The nucleic acids derived from the different organs agree well in elementary composition, although slight variations in the nitrogen and phosphorus occasionally occur. The average yields from 5 kilos. of the various organs vary from 150 grms. from thymus gland to 18 grms. from liver. The product is analysed by suspending 50 grms. of nucleic acid in 500 c.c. of 95 per cent. methyl alcohol and passing hydrochloric acid gas through the suspension for two hours, during which period the organic acid dissolves and the hydrochlorides of adenine and guanine gradually separate. After standing over-night, the salts are separated and dissolved in hot water, and the solution is neutralised to Congo red with sodium hydroxide solution, when the guanine is precipitated, together with a small amount of adenine, from which it may be completely separated by a repetition of the solution in hydrochloric acid and re-precipitation. The two filtrates are mixed, and the adenine is precipitated by the addition of picric acid and purified by one recrystallisation from hot 25 per cent. acetic acid. The guanine is dissolved in boiling dilute sulphuric acid and precipitated by the addition of silver sulphate, after which the silver guanine salt is decomposed by means of hydrochloric acid, and the free guanine is reprecipitated by neutralising the clear liquid with 10 per cent. sodium hydroxide solution. Elementary analysis of the bases thus obtained gave results in close agreement with the theoretical values. (*Cf.* Chapman, *ANALYST*, 1918, **43**, 259.)

T. J. W.

Presence of Acetone in Commercial Ammonia. **J. Bougault and R. Gros.** (*J. Pharm. Chim.*, 1922, **26**, 170–171.)—Acetone has been found to be a fairly general impurity in commercial ammonia solution, and this explains the formation of small quantities of iodoform observed in reactions involving the use of ammonia and iodine. Without doubt, error has thus been introduced in the detection of acetone in urine and other physiological products where ammonia has been used.

D. G. H.

Bacteriological, Physiological, etc.

Composition of Camel's Colostrum. **H. L. Fales.** (*J. Biol. Chem.*, 1922, **53**, 339.)—Examination and analysis of colostrum from a Bactrian camel two days after parturition showed the following characteristics: The sample was thick, creamy white in colour, with a bland taste, and was free from any unpleasant odour. The specific gravity was 1.038 and the reaction to litmus slightly amphoteric. Chemical analysis gave the following results: Fat, 7.4; sugar, 4.2; protein, 5.4; and ash, 0.893 per cent. The protein was composed of: Casein, 4.1; albumin, 0.5; and globulins, etc., 0.8 per cent., whilst the ash contained: Lime, 0.272; magnesia, 0.025; phosphoric anhydride, 0.318; potassium oxide, 0.164; sodium oxide, 0.082; and chlorine, 0.128 per cent.

T. J. W.

Experiments on the Isolation of Vitamin B. A. Seidell. (*J. Amer. Chem. Soc.*, 1922, **44**, 2042-2051.)—The following methods are based upon others previously described (*ANALYST*, 1921, **47**, 357, and *U.S. Pub. Health Repts.*, 1922, **31**, 801), and are modified in accordance with recent experience. Yeast is boiled with water for a few minutes and the solid matter is removed by filtration or by centrifuging. The clear filtrate is acidified and is then shaken with fuller's earth, by which the vitamin is adsorbed, the product being named "activated solid." The "activated solid" is vigorously shaken with saturated barium hydroxide solution for a few minutes, after which the solid is removed by rapid filtration, and the filtrate is acidified with sulphuric acid. Excess of barium carbonate is added to the liquid, the mixture repeatedly shaken until neutral to litmus, and the excess of barium carbonate and barium sulphate filtered off, after which the clear liquid is treated with saturated lead acetate solution and again filtered. The lead remaining in solution is removed by saturating the liquid with hydrogen sulphide, and, after filtering to remove the lead sulphide, the liquid is concentrated by rapid distillation under reduced pressure, and finally by exposure in a vacuum desiccator over sulphuric acid. The product obtained is a resinous sticky mass, of which from 8 to 10 grms. are obtained from 300 grms. of "activated solid." This product is dissolved in water and precipitated successively with saturated silver nitrate solution and ammoniacal silver nitrate solution, the silver being subsequently removed from the precipitates and the final solution by precipitation with hydrogen sulphide. The four fractions were examined by estimating the total solids and nitrogen, and the antineuritic activity by administration to pigeons fed upon a diet of polished rice. The relative protective doses of the solids present in the various solutions were in the following ratios: Original dried extract, 7.5; silver nitrate precipitate, 5.0; ammoniacal silver nitrate precipitate, 3.0; and material not precipitated by silver nitrate, 15(?). The silver precipitates together contain over 50 per cent. of the active vitamin present. The extracts when freed from silver retain their activity indefinitely, whether in the dry condition or in aqueous solution. Since the vitamin in aqueous solution diffuses completely through a collodion membrane, the vitamin molecule is probably of relatively simple constitution. From the nitrogen content it is deduced that the highly active fractions contain vitamin and one or more analogous bases which are not separated by silver precipitation.

T. J. W.

Existence of a Vitamin which promotes Calcium Deposition. E. V. McCollum, N. Simmonds, J. E. Becker and P. G. Shipley. (*J. Biol. Chem.*, 1922, **53**, 293-312.)—By feeding rats upon a basal diet to which various oils and fats were added the authors have shown that not all of these substances are equally efficient in the cure of rickets, of xerophthalmia and of retarded growth. Cod liver oil oxidised by bubbling air through the heated oil for several hours does not cure xerophthalmia, owing to the destruction of vitamin A, but retains its capacity for inducing the deposition of calcium in rachitic animals. Coconut oil contains no vitamin A, and is without effect upon xerophthalmia, but stimulates the

deposition of calcium. Cotton seed, maize, sesamé and olive oils do not cure xerophthalmia, neither have they any effect upon the utilisation of calcium. Butter fat contains the substance stimulating calcium deposition, but in much smaller amounts than do the fish oils examined. The results obtained indicate that the substance causing calcium deposition is a new vitamin controlling the metabolism of the bones and distinct from vitamin A. T. J. W.

Variations in Bacteria Counts from Milk as Affected by Media and Incubation Temperature. G. C. Supplee, W. A. Whiting and P. A. Downs. (*Cornell Univ. Agric. Exper. Stat., Memoir 43, 1921.*)—It does not seem possible to find a combination of temperature and media suitable in all cases for determining the maximum bacteria counts from miscellaneous samples of milk. Incubation on plain agar at 37° C. is the least favourable combination for the purpose; lactose agar at 37° C. is but little better, but dextrose agar at the same temperature has distinct advantages. For developing maximum counts it would appear that dextrose agar at 30° C. for five days is superior to any of the other combinations, and this medium at 20° C., for five days is also superior to plain or lactose agar at either 30° C. or 20° C. W. P. S.

Colorimetric Estimation of Chlorides in Blood. M. L. Isaacs. (*J. Biol. Chem., 1922, 53, 17-19.*)—The proteins in the blood are precipitated with tungstic acid, as in the Folin and Wu method (*ANALYST, 1920, 45, 227*), and 10 c.c. of the filtrate are transferred to a centrifuge tube and neutralised by stirring into it a pinch of magnesium carbonate, after which a slight excess of precipitated silver chromate is added and the contents of the tube well mixed by stirring. After centrifuging, the clear liquid is decanted through a small filter into a 25 c.c. graduated flask, the residue being treated with 10 c.c. of water, and again centrifuged, and the liquid transferred to the filter. When filtration is complete 1 c.c. of 2 per cent. ammonium hydroxide solution is added to the contents of the flask, and the volume is made up to 25 c.c. The yellow colour, due to sodium chromate, is compared with that of a standard solution containing 0.04 per cent. of potassium chromate. When a depth of standard solution equivalent to the colorimeter standard of 20 is used the amount of chloride in the blood is estimated by the equation:

$$\frac{11.73}{\text{Depth of unknown solution.}} = \frac{\text{Mgrms. of sodium chloride per}}{100 \text{ c.c. of blood.}}$$

The silver chromate used in the estimation is prepared by slowly adding 200 c.c. of 5.5 per cent. potassium chromate solution to 100 c.c. of boiling 10 per cent. silver nitrate solution until the clear solution is slightly yellow in colour, after which the silver chromate is washed with distilled water and dried in the air. The presence of phosphates and other salts in blood has no effect upon the accuracy of the method, and the results obtained are in good agreement with those given by Whitehorn's method (*J. Biol. Chem., 1920, 45, 449*). T. J. W.

Quantitative Estimation of Citric Acid in Urine by the Pentabromoacetone Method. W. B. McClure. (*J. Biol. Chem.*, 1922, 53, 357-363.)—Descriptions are given of experiments designed to eliminate the errors inherent in previous methods. The modification adopted is as follows: Two hundred c.c. of urine are made alkaline to litmus by the addition of 5 per cent. sodium hydroxide solution and filtered. To 150 c.c. of the filtrate 3 grms. of charcoal are added, and the mixture shaken vigorously, without heating, for 1 minute, after which it is filtered. To duplicate 50 c.c. portions of the filtrate 1 c.c. of dilute sulphuric acid is added, and bromine vapour is poured upon the surface of the liquid. If the solution remains clear, 10 c.c. of 50 per cent. sulphuric acid and 3 c.c. of 37.5 per cent. potassium bromide solution are added, and the mixture is heated to 50-55 C. for 5 minutes, after which 20 c.c. of 5 per cent. potassium permanganate solution are run in slowly, with vigorous shaking. To remove the excess of bromine and precipitated manganese dioxide a concentrated solution of ferrous sulphate, acidified with sulphuric acid, is added slowly. The remaining precipitate is transferred to a Gooch filter, dried in a desiccator for 24 hours and weighed, after which the filter is heated overnight in an oven to 100-105° C., cooled and again weighed, when the loss in weight represents the pentabromoacetone volatilised, and this figure $\times 0.464$, with the addition of 5 mgrms., gives the weight of citric acid containing one molecule of water of crystallisation. Estimations made by this method with urine containing known added amounts of citric acid showed a recovery of 93.5 to 107 per cent.

T. J. W.

Hypobromite Estimation of Urea in Urine. M. Janet. (*J. Pharm. Chim.*, 1922, 26, 161-170.)—There are certain drawbacks to the use of sodium hypobromite in the determination of urea, and numerous improvements have been suggested, the most successful being that of Gimbert and Laudet, who use a mercury apparatus allowing of vigorous agitation, and a hypobromite solution prepared by the following modification of Yvon's formula: Five c.c. of bromine are slowly poured into 50 c.c. of a 20 per cent. sodium hydroxide solution cooled in ice, the solution being kept well stirred; afterwards 50 c.c. of water are added. One c.c. of solution (diluted if necessary) in which the quantity of urea is not appreciably greater than 1 per cent., is introduced into Yvon's mercury ureometer, and, by turning the tap, brought into the lower part of the apparatus. The solution is washed 3 times with 6 c.c. of 20 per cent. sodium hydroxide solution, and 5 c.c. of Yvon's hypobromite solution, prepared 1 to 6 days beforehand, then introduced. The apparatus is inverted 20 times, this operation being repeated two or three times, and when the evolution of gas has ceased, the whole is placed in water, and, after the temperature is constant, the volume, temperature and pressure are read, and from the volume a correction of 0.05 c.c. is made for the oxygen dissolved in the hypobromite solution. The concentration of urea is obtained from the formula— $V_t \text{ c.c.} \times (H - F_t)^{mm} \times N_t$, where V represents the volume, less 0.05 c.c.; H and F the atmospheric and water vapour pressure respectively at t° ; and N , a constant for each temperature. Comparative estimations with the above method and with the

Fosse gravimetric method gave results agreeing within 1 to 2 per cent. If the apparatus is vigorously shaken, and a recently-prepared hypobromite solution of Yvon's formula used, and the 6 c.c. of 20 per cent. sodium hydroxide solution added at the moment of estimation, a control test is unnecessary. D. G. H.

Estimation of Uric Acid. H. Jackson and W. W. Palmer. (*J. Biol. Chem.*, 1922, 53, 373.)—The complex solution previously described by the authors (*ANALYST*, 1922, 176) for this estimation may be replaced by the following: The "B" salt is prepared by the method previously given, and 100 grms. are dissolved in about 250 c.c. of alcohol, the solution being filtered and evaporated to dryness, with frequent additions of bromine water to decolorise the salt. A 20 per cent. solution of the salt is prepared, and to each 100 c.c. are added 34 c.c. of a 2.5 per cent. aqueous solution of primary calcium phosphate. This solution may then be used in the same manner as the reagent described in the earlier paper. Should the flocculent precipitate produced in the final coloured solution not disappear, a little more of the above 20 per cent. solution may be added, whilst the development of a crystalline precipitate may be prevented by the addition of more calcium phosphate. T. J. W.

Agricultural Analysis.

Proteins in Maize of High and Low Protein Content. M. F. Showalter and R. H. Carr. (*J. Amer. Chem. Soc.*, 1922, 44, 2019–2023.)—Samples of four varieties of maize were ground to pass a 40-mesh sieve, and the various proteins present were extracted by means of water, 10 per cent. sodium chloride solution and 90 per cent. alcohol. The water-soluble proteins were separated by treating the aqueous solution with alkaline copper sulphate solution, and the albumin nitrogen estimated in the residue and the amide nitrogen in the filtrate. Maize of high protein content shows a higher percentage of the total protein to consist of zein and globulins and a smaller percentage of glutenin, amides and albumin than that of low protein content. After hydrolysis with 35 volumes of 20 per cent. hydrochloric acid and boiling for 48 hours (after which the amino acids were estimated by the van Slyke method) *J. Biol. Chem.*, 1911–12, 10, 12, 15 and 275), the specimens of high protein content were found to yield a lower percentage of melanin nitrogen and of non-amino nitrogen in the filtrate from the bases, but a higher percentage of di-amino acid nitrogen than did the specimens of low protein content. The values obtained for zein averaged 50.28 per cent. in high nitrogen maizes, and 31.85 per cent. in those of low protein content. The proportion of the embryo to the whole corn in high protein maizes is about 15 per cent., whilst in Dent maizes this figure is approximately 11 per cent. T. J. W.

The Seeds and Fruit of Certain Field-Weeds. J. Greger. (*Zeitsch. Unters. Nahr. Genussm.*, 1922, 44, 70–80.)—A detailed and illustrated account is given of the morphology and microscopic characters of the seed and fruit of *Fumaria* and *Gallium*, which weeds are sometimes found in feeding stuffs. The diagnostic characters of powdered *Fumaria officinalis* are sufficiently well marked to render it

easy of detection in quite small quantities; these are, the thick-walled warty epidermis, the stone cells, the irregular-shaped endocarp and the pigment cells. A section of the outer coat of the fruit consists of a thick and warty epidermis, under which is a layer of parenchyme with thick fibres connected with the schlerenchyme, and under this are two rows of bast fibres, followed by endocarp. The seed coat shows characteristic pigment cells, under which is a layer of parenchyme, and then compressed perisperm. The alkaloid in *Fumaria* is associated with the pigment. In the endosperm, which contains a very small embryo, the peripheral cells are flattened and the central ones are polygonal and well filled with aleurone and fat. Five varieties of *Gallium* are described—*G. aparine*, *G. boreale*, *G. verum*, *G. asperum*, and *G. mollugo*. *G. boreale* has large, and *G. aparine* small, papillæ and trichomes which cover almost the whole surface; the epiderm at the base of the trichome is raised in *G. aparine*, but not in *G. boreale*. *Gallium verum*, *asperum* and *mollugo* closely resemble one another, but may be identified by the average dimensions of the cells shown in the following table. When boiled with a 5 per cent. solution of potassium hydroxide, *G. boreale* gives a yellowish-brown, *G. verum* gives a dark brown, and *G. mollugo* a light brown colour.

	Epidermis	Parenchyme	Raphide Utricles	Endocarp
<i>G. aparine</i>	65 × 100 μ	170 × 65 μ	160 × 55 μ	170 × 14 μ
<i>G. boreale</i>	25 × 35	80 × 40	300 × 35	140 × 7
<i>G. verum</i>	35 × 100	110 × 27	460 × 27	95 × 14
<i>G. asperum</i>	45 × 80	50 × 80	340 × 27	160 × 14
<i>G. mollugo</i>	50 × 100	60 × 110	350 × 45	75 × 5

H. E. C.

Organic Analysis.

Modified Schiff's Reagent. E. Wertheim. (*J. Amer. Chem. Soc.*, 1922, 8, 1834.)—The advantages claimed are that the solution will not stain the hands, is easily prepared, and that no precautions are necessary for preserving it (it may be put in clear glass bottles and left unstoppered in the light). A cold solution of rosaniline hydrochloride, containing 5 mgrms. in 300 c.c., is treated with 6 grms. of sodium hyposulphite ($\text{Na}_2\text{S}_2\text{O}_4$). This completely dissolves in a few minutes. If the solution is now boiled for one minute, it first becomes red and then practically colourless. It is now ready for use and may be heated in testing for aldehydes, in order to hasten the test, the time being about one half that necessary for the ordinary Schiff test. R. F. I.

Estimation of Water-soluble Matter in Vegetable-tanned Leathers. Chater and Woodroffe. (*J. Soc. Leather Trades' Chem.*, 1922, 8, 247.)—The official method for this estimation, as laid down by the Society of Leather Trades' Chemists, requires the fat-free leather to be soaked in water overnight, and then extracted in such a way that one litre of water at 45° C. percolates through the leather in 3 hours. The authors give curves and tables showing that this treatment does not remove all the water-soluble matter, the method being in error to

the extent of 10 to 30 per cent. of the true figure. They recommend, after the one litre has been extracted, that an extra litre should be extracted at the same temperature; and, although this method does not give an accurate result, it is a great improvement on the present method.

R. F. I.

Determination of the Three Dissociation Constants of Citric Acid.

A. B. Hastings and D. D. van Slyke. (*J. Biol. Chem.*, 1922, **53**, 269-276.)—Electrometric titrations of citric acid solution containing graduated amounts of *N* sodium hydroxide solution, the construction of a curve plotting the P_H values obtained against the sodium hydroxide added in mols. per litre, and the application of formulæ developed by one of the authors in a previous paper (*J. Biol. Chem.*, 1922, **52**, 525), have resulted in the determination of the three dissociation constants of citric acid. These values were obtained by a series of successive approximations, and the first constant is in close agreement with those given by other workers. The following results were obtained: $K_1 = 8.3 \times 10^{-4}$, $K_2 = 4.1 \times 10^{-5}$ and $K_3 = 3.2 \times 10^{-6}$, whilst the corresponding pK values are 3.08, 4.39 and 5.49 respectively.

T. J. W.

Inorganic Analysis.

Use of Mixed Indicators. **A. Cohen.** * (*J. Amer. Chem. Soc.*, 1922, **44**, 1851-1857.)—Among the advantages obtainable by the use of mixed indicators the following are of special importance: (a) the preparation of a mixture which may be adapted to work within any range of P_H value required; (b) obtaining an apparent displacement of the colour changes of an indicator from either half of its working range to the other; and (c) obtaining a more satisfactory colour indication for use with colored solutions. The results obtained with mixed indicators depend upon the P_H value of the liquid under examination, the nature of the indicators employed, and the proportion in which these are mixed. Three mixed indicators are described, designated I., II. and III., the first consisting of equal parts of bromthymol blue and bromcresol purple and showing a blue colour at $P_H = 6.8$, which is not given by any single indicator. This property is of value in the titration of phosphoric and other acids when the solution is yellow in colour, and a sharper end-point is obtained than with bromthymol blue alone. Mixed indicator II. contains equal parts of the monosodium salts of bromcresol purple and bromphenol blue, and shows two ranges of colour: P_H 3.4-4.2 (deep yellow to yellowish-green) and 5.0-6.2 (green-violet). This indicator is superior in the second range of colour to methyl red, *p*-nitrophenol and bromcresol purple, especially with coloured solutions. Mixed indicator III. is composed of the monosodium salts of bromphenol blue and cresol red in the proportion of 2:1, and shows three well-defined colour ranges: P_H 4.6-6.8 (green-blue), 6.8-7.6 (blue-purple), and 7.6-8.8 (purple-violet). This indicator may sometimes be applied to the qualitative detection of the purity of a substance, for a solution of definite concentration will give a certain Sørensen value which will frequently be affected by the presence of impurities. Experiments are described showing the application of these indicators, and several tables showing the relations between them and various single indicators are provided.

T. J. W.

Colorimetric Estimation of Hydrogen Peroxide. M. L. Isaacs. (*J. Amer. Chem. Soc.*, 1922, 8, 1662.)—The following method is short and accurate, and can be used with much smaller amounts of peroxide than are required for the permanganate method. Thirty c.c. of water, 10 c.c. of a 5 per cent. solution of citric acid, and 1 c.c. of the peroxide solution to be tested are placed in a 50 c.c. graduated stoppered flask. After mixing, 1 c.c. of a 10 per cent. solution of ammonium molybdate is added, the solution diluted to the mark and mixed thoroughly. The immediate formation of a yellow colour enables a colorimetric estimation of the peroxide to be made. For a permanent standard, potassium chromate solution can be used (0.4 gm. per litre). Variations in the room temperature are unimportant, but the reagents must be added in the order given.

R. F. I.

[It must not be overlooked that phosphoric acid is frequently added as a preservative to hydrogen peroxide.—EDITOR.]

Volumetric Estimation of Antimony and Tin in Copper Alloys. F. J. Mück. (*Chem. Zeit.*, 1922, 46, 790.)—Two grms. of drillings are dissolved in 20 c.c. of strong nitric acid; the solution is evaporated to 5 c.c., antimony and tin being precipitated. The liquid is diluted to 100 c.c. and boiled 5 minutes, and the precipitate is left to settle, filtered off, and washed four times with hot 5 per cent. nitric acid. The filter and precipitate are transferred to a 700 c.c. conical flask and treated with 15 c.c. of strong sulphuric acid; when the paper is oxidised, 10 c.c. of strong nitric acid are added and the whole gently boiled till clear, with the addition of a little more nitric acid, if necessary. Potassium sulphate (2 to 3 grms.) and tartaric acid (0.5 gm.) are introduced, and the liquid boiled over a free flame till syrupy. After cooling, the mass is taken up in 180 c.c. of water and 7 c.c. of strong hydrochloric acid, the liquid boiled 5 minutes, cooled, and the antimony titrated with permanganate solution. For the estimation of tin the liquid is diluted with 30 c.c. of water and 60 c.c. of strong hydrochloric acid, boiled 15 to 20 minutes with 2 to 3 grms. of powdered antimony, cooled under carbon dioxide, and titrated with iodine solution.

W. R. S.

Rapid Analysis of Ferro-tungsten. L. Losana and E. Carozzi. (*Giorn. Chim. Ind. Appl.*, 1922, 4, 299-301.)—For the rapid industrial control of the percentage of tungsten in iron alloys and tool steels, the following method, occupying less than two hours, gives excellent results. The alloy is powdered and 0.5 gm. heated cautiously with 10 c.c. of nitric acid (sp. gr. 1.2) and about 2 c.c. of hydrofluoric acid. When the metal is entirely dissolved, 5 c.c. of concentrated sulphuric acid are carefully added and the dish heated on asbestos card until white fumes have been copiously emitted for some minutes. When the hydrofluoric acid has been eliminated in this way, the liquid and the adherent precipitate are boiled briskly for 10 minutes with 15 c.c. of concentrated hydrochloric acid; if the nitric acid has been completely expelled, this operation may be carried out in the platinum dish. The liquid is filtered and the precipitate washed with hot 5 per cent. hydrochloric acid solution until the washings cease to contain iron, the wet precipitate

and filter paper being calcined in a platinum crucible and weighed as WO_3 ; multiplication of this weight by 0.7931 gives the metallic tungsten.

An alternative method consists in estimating the tungsten volumetrically in the following manner: After the solution of the metal has been treated with sulphuric and hydrofluoric acids, it is filtered through asbestos in a Gooch crucible, and the precipitate washed with 5 per cent. potassium chloride solution until perfectly neutral. The filter and precipitate are heated, but not boiled, in a beaker for 10 minutes with excess of standard sodium hydroxide solution, and the excess of the alkali estimated by titration in presence of phenolphthalein. The filtrate from the tungsten trioxide may be used for the estimation of the iron, manganese, calcium, phosphorus, aluminium, etc., by the ordinary methods. T. H. P.

Separation of Aluminium and Iron by means of *o*-Phenetidine. K. Chalupny and K. Breisch. (*Zeitsch. angew. Chem.*, 1922, 35, 233–234.)—A method for the quantitative separation of aluminium from iron is based on the fact that aluminium salts are precipitated completely by *o*-phenetidine, whilst iron in the ferrous state remains in solution. Ferric salts, if present, must be reduced before the addition of the reagent, and, to effect this, the solution containing the iron and aluminium salts is acidified slightly with hydrochloric acid and treated for ten minutes with a current of hydrogen sulphide; carbon dioxide is then passed through the solution until all excess of hydrogen sulphide has been expelled. Ammonium carbonate is added until a precipitate forms; this is dissolved by adding a small quantity of dilute hydrochloric acid, the solution is treated with an excess of 5 per cent. alcoholic *o*-phenetidine solution, and the flask containing the mixture is closed and placed in a water-bath at 60°C . The precipitate which forms is collected, ignited, and weighed as Al_2O_3 . For the analysis of alloys in which aluminium is associated with copper and other metals the copper must be separated electrolytically, the iron and aluminium then precipitated as basic acetates, the precipitate dissolved in dilute hydrochloric acid, and this solution treated with *o*-phenetidine solution for the precipitation of the aluminium. W. P. S.

Test for Uranium. H. D. Buell. (*J. Ind. Eng. Chem.*, 1922, 14, 593.)—A nitric acid solution of the sample (*e.g.* slag, ore, etc.) is prepared, a large excess of nitric acid being avoided; this solution is treated with an excess of granulated zinc. When all the acid has been neutralised, a yellow deposit appears on the zinc. The reaction, which may be obtained with a solution containing as little as 0.9 mgrm. of uranium per c.c., is not affected by the presence of gold, platinum, thorium, lead, tungsten, titanium, chromium, mercury or copper; iron and vanadium interfere only when present in large quantity. Sulphuric or hydrochloric acid must not be present in the solution. The yellow deposit appears to be $\text{UO}_3 \cdot 2\text{H}_2\text{O}$.

W. P. S.

Qualitative Separation of Alkaline Earth Metals. M. Polonovsky. (*Bull. Soc. Chim.*, 1922, 31, 806–810.)—The ammonium carbonate precipitate is dissolved in dilute acetic acid, and the solution boiled to eliminate carbon dioxide,

and neutralised with ammonia. Five c.c. are treated with equal volumes of 60 per cent. alcohol and a filtered saturated solution of sodium thiosulphate in 30 per cent. alcohol (75 grms. per litre). In presence of barium a precipitate is immediately obtained, the precipitation being promoted by vigorous shaking. After 10 minutes' standing, the liquid is filtered, and the last of the barium precipitated in 10 c.c. by means of 1 c.c. of 0.7 per cent. potassium sulphate solution. The filtrate is treated with half its volume of a 0.33 per cent. solution of sodium sulphite in 30 per cent. alcohol; strontium is detected by the formation of a milky precipitate which settles readily. The precipitation of strontium is completed by the addition of strong sodium sulphite or potassium sulphate solution. The filtrate is tested for calcium by acidification with acetic acid and addition of ammonium oxalate.

W. R. S.

Rapid Estimation of Sulphur. L. Losana. (*Giorn. Chim. Ind. Appl.*, 1922, 4, 297-299.)—The method previously described (*ANALYST*, 1922, 365) has now been applied to pyrites, copper pyrites, and other mineral sulphides, ultramarine, adulterated white lead, cement, various rocks, sulphates of copper, sodium, etc., naphtha, anthracene, coke, ichthyol, "saccharin," ebonite and caoutchouc, and found to give good results in all cases.

T. H. P.

Estimation of Sulphides by Oxidation with Ferric Sulphate. P. P. Budnikov and K. E. Krauze. (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1921, 4, 157-159.)—The method described, which is applicable to sodium, calcium and zinc sulphides, but not to copper, lead, silver and other insoluble sulphides, is based on the reactions, $3\text{Na}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 = 3\text{Na}_2\text{SO}_4 + 2\text{FeS} + \text{S}$ and $2\text{FeS} + 2\text{Fe}_2(\text{SO}_4)_3 = 6\text{FeSO}_4 + 2\text{S}$; the ferrous sulphate formed is estimated by titration with permanganate solution. In neutral aqueous solution the ferric sulphate undergoes hydrolysis, whilst in presence of acid the sodium sulphide may be attacked and hydrogen sulphide lost; these disturbances are avoided by addition of sodium carbonate or hydroxide, and by acidifying with phosphoric acid after the oxidation.

T. H. P.

Detection of the Nitrous Anion. P. Falciola. (*Gazz. Chim. Ital.*, 1922, 52, II., 87-89.)—Nitrites may be tested for by means of the following reactions: (1) If sodium thiosulphate solution, suitably of $N/2$ concentration, is added drop by drop to an alkali nitrite solution acidified with sulphuric acid, a transitory yellow coloration, varying in intensity with the proportion of nitrite present, appears. This reaction is shown by $N/10,000$ nitrite solution. For moderately concentrated nitrite solution, use may be made of thiosulphate test-paper, which is dipped into the nitrite solution and then into dilute sulphuric or acetic acid. (2) A litre of water, treated with about 2 c.c. of sulphuric acid and then with excess of thiocyanate and about 0.1 gm. of ferrous sulphate, develops an orange coloration, readily if the water contained 0.0001 per cent., and more slowly if it contained 0.00001 per cent., of sodium nitrite. If pure ferrous sulphate is not available, a small piece of iron may be placed, together with dilute sulphuric

acid, in a small glass tube sealed at one end; to the water to be tested are added first a pinch of thiocyanate and immediately afterwards the small tube. The presence of nitrite is indicated by the appearance of the characteristic coloration in the neighbourhood of the tube (*cf.* Horst, *ANALYST*, 1921, **46**, 341). (3) With excess of aniline phosphate, either solid or freshly dissolved or in a solution which has been kept in a closed vessel, 0.1 per cent. sodium nitrite solution gives a yellow coloration changing to a reddish tint, and a 0.01 per cent. solution a faint yellow colour; the limit of sensibility of the reaction does not exceed 0.001 per cent. The coloured substance is removed when the liquid is shaken with benzene, and addition of sulphuric acid changes the colour to red or pink; the latter change does not occur with the yellow coloration obtained with hydrogen peroxide or a persulphate.

T. H. P.

Apparatus, etc.

Apparatus of Transparent Bakelite for Measuring Hydrofluoric Acid.

L. J. Curtmann. (*J. Ind. Eng. Chem.*, 1922, **14**, 610.)—Graduated cylinders made of transparent bakelite will be found useful for measuring hydrofluoric acid; the material is not attacked by the acid, is transparent, less brittle than glass, non-inflammable, and is not softened or distorted when treated with hot water. The material has other uses where the handling of hydrofluoric acid is concerned.

W. P. S.

Cleaning Aluminium Vessels. **B. Seligman and P. Williams.** (*Chem.*

Trade J., 1922, 352.)—The addition of a small amount of sodium silicate entirely prevents the action of hot sodium carbonate solution upon aluminium. For example, the solvent action of a 5 per cent. sodium carbonate solution is immediately arrested by adding an amount of sodium silicate equal to 1 per cent. of the alkali salt present.

Reviews.

NOTES ON QUALITATIVE ANALYSIS [Supplement]. By H. J. H. FENTON, D.Sc., F.R.S. Cambridge University Press, 1922. Price 3s. 6d. net.

Dr. Fenton's well-known book, many times reprinted, has been extensively used by students for nearly forty years. With a view to increasing the usefulness of the volume to more advanced students the author has now added this supplement, which extends the scope of the work so as to include the rarer elements and less common acid radicals and organic compounds. The first twenty pages are devoted to the rarer metals and some of their derivatives. After indicating the groups in which these elements are precipitated in the ordinary course of analysis, a brief description is given of the chief physical constants and chemical reactions of each. The ten following pages give an account of a number of inorganic compounds and acid radicals.

The organic section adds about forty substances to the list; they are given simply in alphabetical order, without any attempt at classification; the selection is

quite arbitrary, and includes a number of compounds useful as drugs, reagents and photographic developers. Finally, there is a list of the solubilities of the principal reagents.

This supplement may be of value to students of university standing; it is mainly outside the range of school teaching, and its scope is hardly sufficiently extensive for it to be regarded as a work of reference in regular analytical practice. Those who are familiar with the original book will know what to expect in the supplement, for the general style of both is the same; the clear presentation of the subject-matter and the good quality of the printing leave nothing to be desired.

A. F. KITCHING.

TRATTATO DI CHIMICA ANALITICA APPLICATA. Vol. II. By G. VITTORIO VILLAVECCHIA. Second Edition. Pp. xvi. + 829. Milan: Ulrico Hoepli, 1922. Price 58 lire.

The publication of a second edition of this book, only five years after its first appearance, is evidence of the favour with which it has been received.

The arrangement of subjects in the new edition is slightly different from that originally chosen, but the general features have been retained. As regards the actual matter, no drastic alterations have been made, the bulk of the text being virtually identical with that of the former edition, although small emendations and additions have been introduced throughout.

The aim of the author has been to give, not all the methods which have been proposed for any particular estimation, but the one or two methods which have been found by experience to yield trustworthy results of sufficient accuracy for the purpose in view. There has been no intention to cater for the beginner, but the practised analyst will find the book useful to refer to concerning subjects with which he may not be brought into intimate contact in the course of his daily work.

The ground covered is extensive and includes: Foods and other commodities containing starch; sugars, and products containing them, such as preserves, sweet-meats, honey, etc.; beer; wine, vinegar; spirits and liqueurs; flesh foods; milk and its products; fatty substances; commercial products derived from fats; essential oils; turpentine, etc.; varnishes; rubber and gutta percha; tanning materials; inks; leather; organic dyestuffs; textile fibres, yarns and fabrics.

In dealing with subjects differing so widely, Professor Villavecchia, who is at the head of the Italian Customs Laboratory, has availed himself of the assistance of a number of experts in the various branches of analysis, and with most of the sections the treatment is satisfactory. The methods given are largely those accepted officially in Italy, and, as might be expected, prominence is often accorded to the work of Italian chemists. A treatise of such comprehensive character does not lend itself to detailed criticism within the space of a review. It should, however, be pointed out that, in some cases, the procedure recommended might with advantage be replaced or modified in accordance with that in vogue in other countries, although the number of such cases is less than in the first edition.

The volume is illustrated with 113 figures in the text, and with 11 plates depicting various starches and textile fibres. An index to the two volumes is included. The book is well printed, and, at the price demanded, cannot be regarded as expensive.

T. H. POPE.

PROTEINS AND THE THEORY OF COLLOIDAL BEHAVIOUR. BY JACQUES LOEB. (International Chemical Series.) Pp. xi. + 293. 80 illustrations. London: McGraw-Hill Book Co. Inc. 1922. Price 15s. net.

During the last decade the subject of colloid chemistry has made exceedingly rapid progress. The interesting and significant thing is the unexpected direction which this advance has taken. We are here referring more particularly to electrolytic colloids, that is, colloidal material which has the property of ionisability—although even this restriction may ultimately be found unnecessary if *all* colloids turn out to be electrolytic in behaviour. It would be rash, however, to make so sweeping a generalisation at the present time. But even accepting the restriction, we are dealing, nevertheless, with an extensive field covering substances of the very first importance. The advance which has been made in this field is due mainly to the work of Pauli and of Loeb on the proteins, of McBain on the soaps, and of Donnan on the theory of membrane equilibrium.

The book before us gives in a clear and concise fashion an outline of what has been accomplished in the case of the proteins. The work cited is mainly the author's own, and the account is marked by those characteristics which are found alone in a first hand and authoritative treatment.

Briefly, the advance consists in the demonstration that electrolytic colloids are to be treated in the first place in precisely the same manner as we would treat crystalloidal electrolytes. Their behaviour is to be considered in the light of the well-known laws and facts of ionisation and ionic equilibria. In the second place the colloidal characteristics are to be taken account of by means of Donnan's theory of membrane equilibrium, which not only allows for ionisation, but at the same time shows in a quantitative manner how the colloidal state brings in certain definite modifications not found in the crystalloidal. Loeb's book, which is divided into two parts, furnishes very conclusive evidence, on the one hand, of the essentially stoichiometrical character of the reactions of proteins, and, on the other, of the direct applicability of Donnan's theory to the explanation of the various properties of these colloidal solutions which, without the theory as a guide, would appear to be wholly chaotic and arbitrary. The key to the whole thing is the recognition of the fact that proteins are amphoteric electrolytes, *i.e.*, electrolytes functioning both as acids and bases, and the further recognition that the behaviour of such substances will be mainly determined by the hydrogen ion concentration (or rather the hydrogen ion activity) obtaining in the system. By pursuing this idea logically, Loeb has succeeded in showing, for example, the true meaning of the iso-electric point, and in clearing up the mystery of the Hofmeister ion series. The introduction of Donnan's theory permits of a proper understanding of such subjects as the origin of the electric charge on protein micellæ, and the influence

thereon of acids, bases, and salts, the magnitude of osmotic pressure, and the phenomena of swelling and of viscosity. In fact, the whole book may be regarded as the most valuable commentary we possess at the present time on the applicability of Donnan's theory of membrane equilibria.

The subject of colloids is so far-reaching that nowadays scarcely any chemist, whatsoever the nature of his own special work, can afford to remain unfamiliar with it. On this ground Loeb's book can be warmly recommended, not only to physiologists, bacteriologists, and bio-chemists, but to a much wider circle of readers.

W. C. McC. LEWIS.

METALLOGRAPHY. By CECIL H. DESCH, D.Sc., Ph.D. Third Edition. Pp. x. + 440. With 14 plates and 105 diagrams in the text. London: Longmans, Green & Co. 1922. Price 16s. net.

Metallography, a word at least 200 years old, literally means the description of metals and their properties, but is now used in a much more restricted sense to signify the study of the internal structure of metals and alloys and its relation to their physical and mechanical properties. The pioneer in this branch of applied science was the late Dr. Sorby, of Sheffield, who devised the methods by which the structure of metals is revealed by means of the microscope, but so little was the practical importance of his work realised at the time that for 20 years it lay almost neglected. Nowadays no progressive metallurgical or engineering works can afford to be without its metallographic equipment and expert staff. The literature of the subject has become very voluminous, and among the standard text-books, that of Dr. Desch, first published in 1910, is one of the best known. It is a difficult book to review, owing to the complexity of the subject and the attempt which has been made to compress into a volume of very moderate size knowledge which covers so wide a field. No author is more competent than Dr. Desch to have undertaken this difficult task, and he has dealt with the theory of the subject in a masterly manner. His work is primarily a text-book for the student, but is of great value to all workers in the subject, owing to the very complete references to the literature. One feels that little, if any, work of importance has escaped the author's notice, and the reader who wishes to know what has been done in his particular section of the subject may be fairly sure of finding the necessary information by reference to Dr. Desch's book.

As this work has not been previously reviewed in the *ANALYST*, a brief epitome may be given. After a brief historical introduction, the author devotes four chapters to a detailed discussion of the diagram of thermal equilibrium, one chapter to practical pyrometry and thermal analysis, and in a later chapter he describes in detail the construction and meaning of the equilibrium diagram of a series of alloys. The methods of preparation and examination of micro-sections are described in two chapters, but no reference is made to the recently developed methods of examining sections of large area by the process of macro-etching. Other chapters are devoted to the crystallisation of metals and alloys, the nature and formation of eutectics, the phenomena of undercooling, the metastable state

produced by quenching from a high temperature, solid diffusion, physical properties, including a good section on hardness, electromotive force and corrosion, the molecular condition of metals in alloys, the nature of intermetallic compounds, plastic deformation, etc. The metallography of iron and steel and of industrial alloys is briefly discussed in two separate chapters, and a complete list of the binary and ternary systems of which equilibrium diagrams have been published is given in an appendix. This third edition does not differ from the first in plan and general arrangement, and the size of the book has increased by only about eleven pages, notwithstanding the rapid growth of the literature. The revision has chiefly consisted in emendations of, and a few additions to, the text, and the completion of references. One therefore finds only brief references to some of the important work of recent years.

Whatever reasons there may be for keeping this volume within its present limit of size, the reviewer suggests that some considerable expansion will be desirable in future editions. On such subjects as grain-growth, recrystallisation, season cracking, etc., references to the literature do not help the reader so much as a clear account by the author, and his reasoned views on the subject.

L. ARCHBUTT.

DOCUMENTS AND THEIR SCIENTIFIC EXAMINATION. By C. AINSWORTH MITCHELL, M.A., F.I.C. Pp. xii.+215. London: Charles Griffin & Co. 1922. Price 10s. 6d. net.

The sub-title explains that the book has especial reference to the chemistry involved in cases of suspected forgery, the investigation of disputed documents, handwriting, etc.

As the Preface states, the scientific examination of documents as a branch of forensic chemistry has been strangely neglected, but fortunately there has been a welcome development in the study of this subject during the last few years, and Mr. Mitchell has been one of the pioneers of the movement by his study of inks, pencil marks, finger prints on documents, etc., the results of which have been published in various scientific journals. The volume under review, therefore, is by one who is a recognized authority, and Mr. Mitchell's latest contribution to the subject will be welcomed by, and is strongly recommended to, all who are called upon at any time to examine documents critically and to pass judgment upon them, whether they be chemists, lawyers, or business men, though naturally the book will appeal especially to the document expert.

The book deals with the scientific examination of paper, pens, pen markings, ink on documents, pencils, pencil markings, handwriting, secret writing, type-writing, printing, stamps, seals, envelopes, and finger prints on documents, and contains a large number of illustrations. It not only summarises our present knowledge of the subjects treated, but also gives the results of the author's own extensive investigations and experience, a great deal of this matter being new and not previously published. The fact that the book is the work of an expert with wide experience, and that it abounds in practical details, the methods and apparatus

used being described in full, makes it a most valuable contribution to the literature of forensic chemistry.

It is fitting that such a matter as "Documents" should be dealt with by a chemist, as, apart from handwriting, it is essentially a chemical subject, including as it does the chemical analysis of paper, ink, pencil marks, sealing wax and adhesives on envelopes, as also the chemical treatment of paper for the development of secret writing and finger marks. The value of the chemist in this connection was recognised to some extent during the war.

The chapter on handwriting is particularly welcome, as the comparison of writings is a subject which has been greatly and undeservedly neglected by scientific men, who have generally relegated it to the same category as character reading from handwriting, palmistry and phrenology; and so, until recently, it has been bound up in the bundle of the scientifically damned. There are still handwriting experts who are not scientific, but by the help of such books as Osborn's standard work and of the present volume, the subject is being rescued from unmerited reproach and placed in the position it should justly occupy.

The book is well arranged and clearly printed, and, not only the author, but also the publisher and printer, are to be congratulated. It is strongly recommended to all who are interested in the subject, and will prove indispensable to the document expert.

A. LUCAS.

Publications Received.

TESTED METHODS OF NON-FERROUS METALLURGICAL ANALYSIS. By S. PILE and R. JOHNSON. Pp. 127. London: H. F. & G. Witherby. 1922. Price 7s. 6d. net.

LABORATORY MANUAL OF COLLOID CHEMISTRY. By H. N. HOLMES. Pp. xii. +127. London: Chapman & Hall. 1922. Price 10s. net.

INTRODUCTION TO THE CHEMISTRY OF PLANT PRODUCTS. By P. HAAS and T. G. HILL. Vol. II., pp. viii. +140. London: Longmans. 1922. Price 7s. 6d. net.

THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES. E. J. PARRY. 2 Vols., pp. 549 and 364. London: Scott, Greenwood & Son. 1922. Price, Vol. I., 30s. net. Vol. II., 21s. net.

BOILER FEED WATER. By P. G. JACKSON. Second Edition. Pp. xi. +143. London: Chas. Griffin & Co. 1922. Price 5s. net.

A concise description of the effects, treatment and analysis of water for boiler-feeding purposes.

SCALES FOR FINDING METRIC EQUIVALENTS AND MENSURATION RESULTS. A. E. BAWTREE, 7, Manor Park Road, Sutton. Price 1s. post free.

Sixteen scales on inside of folding card (5 in. x 4 in.). Into their metric equivalents Nos. 1, 2 and 3 convert miles, yards and inches; Nos. 4, 5, 6 and 7 convert square yards, square inches, cubic yards and cubic inches; No. 8 deals with pressure in lbs. per square foot; Nos. 9, 10, 11 and 12 deal with tons, pounds, grains and fluid ounces and also indicate gallons. Nos. 13, 14 and 15 compare Fahrenheit and Centigrade thermometer scales over a range from absolute zero to 2,000 deg. C.; No. 16 gives the circumference of a circle when the radius is known, and from this information with regard to spheres, cylinders and cones is readily found.

THE JOURNAL OF THE IRON AND STEEL INSTITUTE. Vol. CV. 1922.

CATALOGUE NO. 7. TECHNICAL AND SCIENTIFIC BOOKS London: W. & G. Foyle.