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THE DENSITIES AND REFRACTIVE INDICES OF THE LEAMINGTON SPA WATER.

By C. H. MANLEY, M.A., A.I.C.

In a pamphlet entitled "The Chemistry of the Leamington Spa Water" (1914) S. Henry Smith remarks that this water is one of peculiar interest as regards its saline constituents. Attention is drawn to the fact that in prehistoric ages the whole of the surrounding district formed the bottom of a large inland sea, which stretched from the Edge Hills to Shuckburgh and Bourton-on-Dunsmore, with an outlet down the Evesham Valley to the Bristol Channel. With the subsequent disappearance of the sea, a huge deposit of saline material covered with silt and earth remained. Surface water gaining access at a later period, a highly saline solution resulted.

The chemical composition of the Leamington Spa water is somewhat complicated. The following figures—the mean of several analyses—are quoted by S. H. Smith (*loc. cit.*):

	Pump Room Supply. Parts per 100,000.	
$BaSO_4$	0·1376	
$SrSO_4$	1·2088	
$CaSO_4$	248·2	
$MgSO_4$	125·604	
MgI_2	0·0032	Traces of manganese and titanium.
$MgBr_2$	0·3354	
$CaCl_2$	58·36	
$MgCl_2$...	47·37	
NaCl	1245·127	
KCl	9·9264	
LiCl	0·0665	
NH_4Cl	0·0742	
$Fe_2(CO_3)_3$	0·286	
$CaCO_3$	4·4	
Silicic Acid	0·8	
Total	1741·8991	

Dried residue at 110° = 1739·0000.

Radium is also stated to be present. No details are given as to the actual methods employed for the chemical analysis, and it is therefore impossible for one to form any true estimate of the degree of accuracy attainable.

In this present paper is given an account of certain determinations both of the relative densities and the refractive indices of the Spa water. The water used was drawn from the Engine House supplying the Pump Room on August 30, 1915, a few gallons of water being allowed to flow away before collecting a sample in a large earthenware jar which had first been rinsed with some of the same water; the jar was then corked, sealed and subsequently removed to Oxford, where the necessary measurements were effected in the Laboratory of Magdalen College. Prior to the measurements some of the water was poured into a Winchester quart bottle and allowed to stand until clear, after which portions for the several determinations were carefully decanted off as required; this plan rather than that of filtration was adopted in order to avoid any possible inaccuracy that might be introduced by the adsorptive properties of filter-paper.

Relative Density of the Spa Water.—For determining the relative densities at the several temperatures named below, a modified form of the well-known Sprengel pyknometer was employed; the instrument was narrow of limb and by actual trial it was found that when charged with water the pyknometer and its contents assumed the temperature of the thermostat within ten minutes after immersion; it was also found possible to adjust the liquid content to within approximately $\frac{1}{5}$ mgrm. The weighings of distilled water and spa water at 15°, 18° and 25° C. were carried out with a high degree of accuracy.

The following are the tabulated mean results:

Temperature.	Distilled Water.		Spa Water.	
	Apparent Weight.	Weight [M] in Vacuo.	Apparent Weight.	Weight in Vacuo.
15° C.	9·7286	9·7402	9·8481	9·8597
18° C.	9·7241	9·7357	9·8425	9·8541
25° C.	9·7102	9·7218	9·8272	9·8388

Temperature.	Density [D] of Water (Despretz).	Volume of Pyknometer [V = M/D].	Density [Δ] of Spa Water.
15° C.	0·9991	9·7490	1·01136
18° C.	0·9986	9·7495	1·01073
25° C.	0·9971	9·7501	1·00910

It will therefore be seen that the above values for the Spa water are in terms of pure water at 4° C., and when plotted graphically, lie on three points of a right line

curve. The coefficients of expansion, k_1 and k_2, of the Spa water between 15° and 18° and 18° and 25° C. respectively were calculated with the aid of the formula

$$k = \frac{d^t/d^\theta - 1}{\theta - t},$$

in which d^t = the density of the Spa water at $t°$,
and d^θ = " " " $\theta°$,
θ being $> t°$.

Accordingly $k_1 = 0{\cdot}00021$
$k_2 = 0{\cdot}00023$
Mean value $k = 0{\cdot}00022$

For pure water, and within the limits of temperature 15°-25°, k, calculated from the values for Δ by Despretz = 0·00021.

The Refractive Indices.—The refractive indices were measured with the aid of a Troughton and Sims refractometer capable of being read to 15″ of arc. A hollow glass prism by Hilger was employed, its refracting angle being equal to 50° 59′ 15″. A number of measurements were carried out, every care being taken to regulate the temperature. The refractive index, μ, in each case was calculated from the usual formula. The values given below are for 15°, 18°, and 25° C. Side by side with these are tabulated figures expressing the refractive indices of highly purified water—the result of measurements which were effected with the aid of a refractometer and quartz prism belonging to the Royal Society. If μ_1 and μ_2 denote the refractive indices of the spa water and purified water respectively, the expression μ_1/μ_2 will represent the relative refractivities for the several temperatures. The importance of a measurement of the relative refractivities and of the relative densities has already been pointed out in regard to the examination of samples of sea-water (J. J. Manley, Proc. Roy. Soc., Edinburgh, 1900, pp. 35-43).

Finally, the application of the formulæ $\frac{(\mu-1)}{d}$ and $\frac{(\mu^2-1)}{(\mu^2+2)d}$ to the values obtained for the densities and refractive indices of the Leamington Spa water at 15°, 18°, and 25° C. shows that the water conforms to the law of Gladstone and Dale on the one hand and to that of Lorentz and Lorenz on the other, constant values obtaining at each of the three temperatures.

Temperature.	μ_1 (Spa).	μ_2 (purified).	μ_1/μ_2.	$\frac{(\mu_1-1)}{d}$.	$\frac{(\mu_1^2-1)}{(\mu_1^2+2)d}$.
15°	1·3363	1·3334	1·0017	0·3325	0·2052
18°	1·3360	1·3333	1·0023	0·3324	0·2052
25°	1·3353	1·3330	1·0040	0·3323	0·2051

In conclusion, I desire to express my thanks to Mr. Charles Ravenhill, Manager of the Leamington Spa Pump Room, for facilities allowed me in collecting the water for the above measurements.

THE VOLUMETRIC ESTIMATION OF LEAD.

By JOHN WADDELL, B.Sc. (Lond.), D.Sc. (Edin.).

Some years ago a method for estimating lead in ores was published in the Transactions of the American Institute of Mining Engineers; but though sound in principle, it was not completely satisfactory on account of several inaccuracies in detail.

The process consists in precipitating the lead as chromate, dissolving in hydrochloric acid, adding potassium iodide, and titrating the iodine set free with sodium thiosulphate. The reaction may be represented by the following equations:

$$2PbCl_2 + 2K_2CrO_4 = 2PbCrO_4 + 4KCl,$$
$$2PbCrO_4 + 16HCl + 6KI = 2PbCl_2 + 2CrCl_3 + 6KCl + 3I_2,$$
$$6Na_2S_2O_3 + 3I_2 = 6NaI + 3Na_2S_4O_6.$$

Thus the equivalent of one Pb is $3Na_2S_2O_3$. A convenient strength of solution of thiosulphate is such that 1 c.c. equals 0·005 grm. of lead. This means that approximately 18 grms. of crystalline sodium thiosulphate per litre should be used.

This method of estimation is excellent from the educational point of view, because the process involves a number of instructive principles, and introduces mass action and the effect of time. The fact that there are, chemically, a number of reactions involved does not detract from its value as a commercial analytical method, because these reactions are for the most part concurrent and not successive; and are, therefore, not tedious.

The process is more delicate than the molybdate method, the end-point is very distinct, and this makes it possible to detect the presence of lead in tailings which do not show any indication of lead by the use of ammonium molybdate. It is most applicable for the most common ore, namely, galena in calcite. This case will be described first.

Into a 250 c.c. Erlenmeyer flask are placed 1 grm. or other quantity of the ore (depending upon its richness in lead); about 10 c.c. of hydrochloric acid are added, and after digestion for a time long enough to get rid of most of the hydrogen sulphide, about 5 c.c. of nitric acid are added, and the solution evaporated until the volume is reduced to about 7 c.c. Ammonia is added until the lead and other insoluble hydroxides are precipitated. If the colour indicates the presence of much iron, care will need to be taken in the next step. Acetic acid is added until the liquid smells strongly of the acid. The precipitate should now be dissolved with the exception of siliceous matter, which, unless it is gelatinous, may be disregarded; 2 or 3 grms. of ammonium acetate may advantageously be added to ensure complete dissolution of the lead. All these operations should be carried out at a temperature near the boiling-point, but if there is much iron present, ammonium acetate may advantageously be added. Care must be taken that no basic ferric acetate is precipitated; the solution must be sufficiently acid and should not be boiled.

The liquid will now measure about 25 c.c. To it is added while hot 10 c.c. of a 10 per cent. solution of potassium chromate (I know of no objection to the dichromate, but I have always used the chromate). This is far more than the calculated amount; but the excess, which is better added all at once, causes the precipitation to be more rapid. The precipitate, often lemon yellow at first, becomes orange in a minute or two, settles readily, and can be filtered in five minutes, especially if it is shaken vigorously from time to time during this period. A reasonably good qualitative filter paper will not allow the precipitate to run through. The filter should be fairly large; 11 cm. in diameter is a convenient size. The clear filtrate that runs through I usually keep by itself in a warm place, to make sure that no more precipitate will form. If the liquid in the flask did not exceed 50 c.c., and if there was not too great an excess of ammonium acetate, the precipitation will be complete.

The potassium chromate is washed out from the flask with boiling water. The first two or three portions of water should contain a few drops of acetic acid, in case iron is present, but the acid should be added only so long as soluble chromate is still visible, for when the potassium chromate has been removed, lead chromate is slightly soluble. Four or five washings of about 10 c.c. or 15 c.c. each should be enough. It is not necessary to remove all of the lead chromate from the flask. Two or three washings of the precipitate on the filter with boiling water should be enough, but the washings must be tested with lead acetate. The whole operation of filtering and washing should not take more than ten minutes, and practice may well reduce the time.

The lead chromate is dissolved on the filter in hydrochloric acid, and the solution collected in the flask, which contains the remainder of the precipitate. For this purpose a considerable quantity of acid must be used, or the subsequent operations will be too slow; but, on the other hand, the acid must not be too concentrated, nor must it be hot, otherwise chlorine will be set free and the chromate in part reduced, which will obviously lead to a low result for lead. About 25 c.c. of acid of 1·18 sp. gr., and 75 c.c. of water, is a suitable solution to use.

It is not necessary that all the lead chloride thus formed on the filter should be dissolved, provided all of the chromic acid is removed; but lest some undecomposed chromate should be occluded in the residue, it is best to dissolve most of the chloride. This can be done by washing alternatively with acid and water; 5 or 10 c.c. of hot water facilitates the solution without endangering loss of chlorine, but the filtrate in the flask must not become perceptibly warm. When the filter has been freed from chromate, any acid left over should be added to the solution in the flask and the solution made up to nearly 200 c.c. with water.

One gram or less of potassium iodide is added to the flask, and so soon as the coloration, due to iodine, appears, the thiosulphate solution is run in from the burette at the rate of two or three drops a second, occasionally shaking the flask gently. If too much iodide is added there will be a precipitate of lead iodide which will slightly obscure the reaction, but with the quantity suggested there should be no precipitate. Theoretically an infinitesimal quantity of iodide would suffice, since by the action of the thiosulphate it is re-formed; but the mass action effect requires about a gram, or the reaction will be too slow.

When the iodine has nearly disappeared and the solution becomes green, due to the formation of chromic salt, a little starch solution is added to the flask, the contents vigorously shaken, and the titration with thiosulphate continued.

A little practice will enable the operator to add nearly the right amount of thiosulphate before adding the starch. The tendency of beginners is to add the starch too soon, and it takes many additions of thiosulphate, with alternate shakings, before the colour shows any change. This makes the process seem unduly long, but with proper manipulation, which is easily acquired, it should take only a short time. When the blue colour has almost disappeared, about 10 c.c. of hydrochloric acid of 1·18 sp. gr. are added, the solution heated to about 40° C., shaken, and if the blue colour has not entirely disappeared, thiosulphate is run in drop by drop, with alternate shaking.

In the duplicate estimation it is not advisable to add approximately, but somewhat less than, the proper amount of thiosulphate, as time is required for the reaction of the iodide and the chromate on the one hand, and the thiosulphate and iodine on the other.

The thiosulphate is conveniently standardised against lead or lead sulphate, which is precipitated as chromate and treated thereafter just like the ore.

If the ore contains antimony, bismuth, silver, or decomposable silicates, the operation is not quite so simple as with the ordinary ores of galena and calcite. The lead in the condition of sulphate is filtered from the soluble sulphates, and then dissolved in ammonium acetate, the rest of the operation being conducted in the manner previously described. In this case the analysis is longer than with ammonium molybdate, the advantage being in the delicacy. In tailings, a fraction of a per cent. may be determined by the chromate method where no lead would be shown by the molybdate method.

A few examples may be given to illustrate the degree of accuracy of the method.

In two estimations, taking 25 c.c. of a pure lead solution containing 0·150 grm. of lead, 30·51 c.c. and 30·65 c.c. of thiosulphate were required. A student in a check determination used 30·50 c.c. of thiosulphate.

A solution of ore was made such that 25 c.c. would require somewhere about 30 c.c. of thiosulphate. In four estimations the figures obtained were 28·73 c.c., 29·25 c.c., 29·25 c.c., and 29·25 c.c. The first result was evidently too low. In a check estimation, in which the chromate was dissolved in 50 c.c. of 1 : 1 hydrochloric acid, 29·04 c.c. and 28·97 c.c. were required. This confirms the 29·25 c.c., as the more concentrated acid doubtless set free a little chlorine.

Four estimations of an ore were made, taking 0·5 grm. for each analysis and requiring 28·30 c.c., 28·40 c.c., 28·28 c.c., and 28·30 c.c. of thiosulphate. The lowest and highest figures gave respectively 27·76 per cent. and 27·88 per cent. of lead.

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ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

FOOD AND DRUGS ANALYSIS.

Estimation of Small Quantities of Alkaloids. E. Carlinfanti. (*Boll. Chim. Farm.*, 1915, **54**, 321-323; through *J. Chem. Soc.*, 1915, **110**, ii., 709-710.)—The estimation of small amounts of morphine or codeine, either in pharmaceutical preparations or for toxicological purposes, may be effected by the following colorimetric methods, a Wolff colorimeter being employed: In the case of morphine, the solution to be examined and a known volume, say 1 c.c. of a 0·5 per cent. morphine hydrochloride solution, are evaporated separately in basins on a water-bath, and allowed to cool in a desiccator. Each of the residues is dissolved in 5 c.c. of concentrated sulphuric acid, and the liquid introduced into a tube holding about 50 c.c. and fitted with a ground stopper; each dish is washed twice with 3 c.c. of concentrated sulphuric acid, and the washings added to the tube, which is then closed and immersed for fifteen minutes in a boiling water-bath. To the cooled tubes are added 10 c.c. of a mixture of 100 c.c. of concentrated sulphuric acid, with 2 drops of nitric acid (sp. gr. 1·4); on shaking the tubes, the characteristic blood-red coloration appears. The solutions are then introduced into the cylinders of the colorimeter, in which they are made up to the same height by addition of the small quantities of concentrated sulphuric acid used for washing the tubes.

In the case of codeine, to each of the two aqueous residues, reduced to about 1 c.c. by evaporation on a water-bath at 70° to 75° C., 15 to 20 c.c. of monohydrated sulphuric acid are added cautiously, so that the mixture is not heated. The liquid is then introduced into a 50 c.c. flask, together with three quantities of 5 c.c. of the acid used to wash out the dish and 10 c.c. of monohydrated sulphuric acid containing 2 c.c. of 10 per cent. ferric chloride solution per 100 c.c. of the acid. After being shaken, the flasks are immersed for fifteen minutes in a water-bath at 80° C., the cooled solutions, which have acquired blue colorations, being introduced into the cylinders of the colorimeter as before.

These methods admit of the estimation of 0·001 to 0·003 grm. of morphine or codeine hydrochloride to within about 0·0001 grm.

Estimation of Small Quantities of Alkaloids. C. Carlinfanti and M. Scelba. (*Boll. Chim. Farm.*, 1916, **55**, 225-232; through *J. Chem. Soc.*, 1916, **110**, ii., 356-357.)—Under the conditions given for the estimation of morphine (see preceding abstract), acetoxy-morphine (heroine) may be estimated with considerable accuracy; it may be distinguished from morphine, since it colours concentrated sulphuric acid containing nitric acid orange-yellow in the cold and blood-red when hot, and does not reduce iodic acid. Codeine may also be estimated similarly, but for very small quantities of this alkaloid the method previously given (*loc. cit.*) is recommended.

Apomorphine may be estimated as follows: 1 to 5 c.c. of a 0·1 per cent. solution of the hydrochloride is evaporated to dryness in a basin on a water-bath. The residue is allowed to cool in a desiccator, and 10 c.c. of 95 per cent. alcohol and 0·1 grm. of sodium bicarbonate immediately added. The whole is then covered with a watch-glass and stirred repeatedly during four to five hours, after which the liquid is poured into a tared flask and made up to volume with the washings of the residue with 95 per cent. alcohol. When the suspended sodium bicarbonate has settled, a portion of the clear liquid is decanted into a colorimeter, and the emerald-green coloration which develops compared with that obtained from a known quantity of the alkaloid treated similarly. This method gives good results with quantities of apomorphine of the order 0·001 to 0·002 grm. For smaller amounts, the authors recommend the following modification of Grimbert and Leclère's method (ANALYST, 1915, **40**, 121): To the solution of the alkaloid, made up with water to 3 c.c., are added 5 drops of saturated mercuric chloride solution and then 5 drops of 10 per cent. sodium acetate solution. The liquid is then boiled for half a minute, cooled, mixed with 1 c.c. of amyl alcohol, and introduced into a 50 or 100 c.c. flask, the vessel being washed out several times with small quantities of 95 per cent. ethyl alcohol, and the volume made up with concentrated alcohol. After being shaken, the liquid is left until the mercurous salt settles, the clear solution being compared in the colorimeter with one prepared similarly from a known weight of apomorphine.

In the case of strychnine, a definite volume of the solution containing at least 0·004 to 0·005 grm. of the alkaloid is heated to boiling with 20 to 25 c.c. of 15 per cent. sulphuric acid solution, recently prepared bromine water being added, drop by drop, until the liquid assumes a pale yellow colour, and the boiling then continued for a few minutes; the presence of strychnine is revealed by a more or less intense reddish-violet coloration. Further addition of a few drops of bromine water turns the hot acid liquid pale yellow, and subsequent boiling renders it reddish-violet again. The cold solution is made up to 50 to 100 c.c., and its depth of colour matched with that of a solution prepared similarly from a known weight of the alkaloid. With a pharmaceutical preparation containing a strychnine salt, a quantity containing at least 0·005 grm. of the base is mixed with an alkali, and the mixture extracted with chloroform, the residue from the latter then being dissolved in 15 per cent. sulphuric acid solution and treated as above.

Under the conditions employed in the case of strychnine, brucine gives a salmon-red coloration with bromine water, but, when the alkaloid is present in small proportion, the second addition of bromine water renders the solution colourless. With strychnine, on the other hand, the violet-red coloration persists almost unaltered after a second and even a third treatment with bromine water. In conformity with this behaviour, the proportion of strychnine in *Nux vomica* preparations and other solutions containing strychnine and brucine in approximately equal proportions may be estimated by means of bromine water in the manner described above.

Colorimetric Determination of Cinnamaldehyde in Cinnamon. T. von Fellenberg. (*Mitt. Lebensmitteluntersuch. Hyg.*, 1915, **6**, 254-266; through *J. Chem. Soc.*, 1916, **110**, ii., 354-355.)—The value of cinnamon lies in its cinnamaldehyde content

rather than in the quantity of total essential oil it contains. A method for the estimation of cinnamaldehyde depends on the coloration which develops when the aldehyde is treated with sulphuric acid and isobutyl alcohol. One grm. of the cinnamon is heated just to boiling for ten minutes with 40 c.c. of 95 per cent. alcohol in a flask attached to a condenser, and any distillate collected in a 100 c.c. flask. From 30 to 35 c.c. of the alcohol are then distilled, 100 c.c. of boiled water are added to the residue, and the distillation is continued until the total distillate measures 100 c.c.; 5 c.c. of the distillate are then mixed with 2 c.c. of 5 per cent. isobutyl alcohol solution (in 95 per cent. alcohol) and 3 c.c. of 38 per cent. alcohol, 20 c.c. of concentrated sulphuric acid are added, and, after forty-five minutes, the coloration obtained is compared with that yielded by a known amount of cinnamaldehyde under similar conditions. The standard cinnamaldehyde solution used for comparison contains 2 per cent. of the aldehyde in 38 per cent. alcohol solution; it may be prepared from the aldehyde-sulphite compound, and standardised by a bromine-iodine titration. Nine samples of Ceylon cinnamon were found to contain from 1·31 to 1·84 per cent. of cinnamaldehyde; seven samples of cassia-cinnamon contained from 1·23 to 2·77 per cent., and a sample of cinnamon flowers 3·73 per cent.

Colour Reaction of Croton Oil. Comte. (*J. Pharm. Chim.*, 1916, **14**, 38-39.)—Croton oil contains an active resinous constituent, which, like the oil itself, is soluble in absolute alcohol, and gives in alcoholic solution a specific colour reaction. The oil under examination is treated with twice its volume of absolute alcohol, and a little of the clear alcoholic solution poured on to a concentrated solution of potassium or sodium hydroxide. A brilliant brownish-red or reddish-violet ring (according to the age or origin of the oil) indicates the presence of croton oil. This reaction is not given by olive, poppy, sesame, castor or cod-liver oils. As a confirmatory test, the skin of the arm may be rubbed with a few drops of the alcoholic solution. After a few hours a vesicular eruption will appear on the part touched.

C. A. M.

Estimation of Essential Oils in Liqueurs. C. F. Muttelet. (*Ann. Falsific.*, 1916, **9**, 17-22.)—According to a recent French regulation, alcoholic beverages must not contain more than 0·50 grm. of essential oils per litre. The author's method of estimation is to mix 200 c.c. of the liqueur with 75 c.c. of water, and distil about 200 c.c. of the mixture. The distillate, containing about 25 per cent. of alcohol, is introduced into a 300 c.c. stoppered flask, which contains 50 grms. of finely powdered recrystallised sodium chloride, and after the addition of 10 c.c. of petroleum spirit the flask is shaken until the salt has dissolved, a few c.c. of water being added if necessary. The shaking is continued for about ten minutes, and the flask then allowed to stand. In the presence of the salt the petroleum spirit is able to extract the essential oils from their alcoholic solution. The saline layer is extracted twice more with, each time, 5 c.c. of petroleum spirit, and the united extracts dried over anhydrous sodium sulphate, and evaporated by passing a slow current of dry air through the flask, which is meanwhile immersed in water at 30° C. The residue is weighed at intervals of five minutes until two consecutive weighings are identical. In test experiments, the loss of essential oil did not exceed 1 to 2 mgrms. C. A. M.

Estimation of Essential Oils in Liqueurs. L. Bonnet. (*Ann. Falsific.*, 1916, **9**, 14-16.)—In testing liqueurs such as anisette and chartreuse 110 c.c. of the sample are mixed with 30 to 40 c.c. of water, and 100 c.c. distilled and mixed with sufficient 95 per cent. alcohol and water to give 150 c.c. of liquid of 50 per cent. alcoholic strength. This is mixed with 40 c.c. of Hübl's iodine solution and left for three hours in the dark at 15° to 18° C., and the iodine absorption estimated in the usual way. The blank consists of 150 c.c. of 50 per cent. alcohol. Test experiments with liqueurs containing known quantities of essential oils showed that the factor for calculating the amount of oils in grms. per litre from the iodine value was 1·515 in the case of anisette and 1·498 in the case of chartreuse. In practice it is advisable to base the coefficient upon the predominating essential oil in the mixture.

C. A. M.

Estimation of the Iodine Value of Essential Oils. R. Marcille. (*Ann. Falsific.*, 1916, **9**, 6-11.)—The influence of light upon the estimation of the iodine value of essential oils has already been pointed out (ANALYST, 1915, **40**, 152). This influence varies in an irregular manner. It lowers the iodine value of most essential oils, but in a few cases, notably aniseed oil, it increases the value. It is advisable to allow the absorption to proceed for twelve to twenty-four hours, parallel estimations being made in the light and in the dark. If the iodine value obtained in the light be greater than that obtained in the dark, it is probable that the mixture contained aniseed or an allied oil. For example, in the dark a sample of aniseed oil gave an iodine value of 1·41 in twenty-four hours, rising to 1·65 after ninety-six hours, whereas in the light it showed 2·03 after thirty minutes, falling to 1·96 after two hours, and 1·79 after seven hours. Since menthol gives no iodine value, it is possible to distinguish between it and peppermint oil. As a rule, in examining liqueurs it is unnecessary to distil the sample, the presence of sugar not interfering with the estimation of the iodine value. In the case of certain absinthes, however, differences were observed in the results obtained before and after distillation. The following are some results recorded by the author. In each case the iodine solution was left in contact with the oil for three hours in the dark at 25° C.

Specific Gravity.	Refractive Index.	Iodine Value.
0·991	1·5609	1·32
0·992	1·5605	1·38
1·003	1·5588	1·18
1·027	1·5518	0·93
1·060	1·5450	0·43
1·078	1·5488	0·30
	1·5480	0·24

The last sample was a Russian oil which had been kept for six months in a corked flask. Originally its iodine value was 1·24. C. A. M.

Estimation of Fat in Cream. L. Lindet. (*Ann. Falsific.*, 1915, **8**, 291-294.)—The author describes a method involving the measurement of the area of the splash of a drop on bibulous paper. W. P. S.

Non-protein Nitrogenous Constituents of Feeding-Stuffs. H. S. Grindley and H. C. Eckstein. (*J. Amer. Chem. Soc.*, 1916, **38**, 1425-1431.)—The various forms of nitrogen not precipitated by colloidal ferric hydroxide from a cold aqueous infusion of a feeding-stuff are given in the following table, the figures expressing percentages on the original material:

	Total Nitrogen.	Humin Nitrogen.	Free Amino-acid Nitrogen.	Free and Combined Acid-amide Nitrogen.	Combined Amino-acid Nitrogen.	Residual Soluble Nitrogen.
Alfalfa hay	0·462	0·038	0·133	0·088	0·082	0·093
Timothy hay	0·132	0·023	0·042	0·023	0·009	0·023
Blood meal	0·262	0·006	0·081	0·067	0·071	0·015
Maize	0·082	0·005	0·031	0·015	0·007	0·015
Clover hay	0·285	0·036	0·091	0·026	0·005	0·088

It is apparent that the non-protein nitrogenous constituents consist largely of the forms of nitrogen that result from the decomposition of proteins by hydrolysis, and it is evident that only a small part, if any, of these constituents can in any way interfere with the application of the Van Slyke method (*cf.* ANALYST, 1915, **40**, 399; 1916, 46) for the estimation of amino acids. W. P. S.

Analysis of Spirit of Peppermint. H. L. Thompson. (*Amer. J. Pharm.*, 1916, **88**, 303-308.)—Fifty c.c. of the sample are mixed with water at about 50° C. in a special flask with a graduated neck, and after standing for about four hours the volume of the separated oil is read directly on the scale. An aliquot portion is withdrawn with a pipette, filtered, and weighed, to obtain the weight corresponding to the volume. The weighed quantity of oil is boiled for an hour beneath a reflux condenser with 25 c.c. of $\frac{N}{2}$ alcoholic sodium hydroxide, and the excess of alkali titrated with $\frac{N}{2}$ hydrochloric acid. The number of c.c. used in the saponification multiplied by 9·9 and divided by the weight of oil gives the percentage of menthyl acetate in the oil. The solution is transferred to a separating funnel, and the residual oil (which contains menthol) is washed two or three times and separated. It is then mixed with 1 grm. of anhydrous sodium acetate and 5 c.c. of acetic anhydride, and boiled for an hour on the sand-bath, after which it is washed in a separating funnel, mixed with about 50 c.c. of water, rendered faintly alkaline to phenolphthaleïn, washed, and separated. A weighed quantity of the acetylated oil is boiled with 25 c.c. of alcoholic sodium hydroxide solution beneath a reflux condenser, and the excess of alkali titrated as before. The number of c.c., multiplied by 7·8 and divided by the weight of oil taken, gives the amount of free and combined menthol in the oil

C. A. M.

Detection of Natural and Artificial Pigments in Oleomargarine and Butter. L. S. Palmer and W. E. Thrun. (*J. Ind. and Eng. Chem.*, 1916, **8**, 614-615.)—The detection of carotin, the natural yellow pigment of animal fats, in oleomargarine is made necessary by the oleomargarine laws of many States. Cornelison's test for carotin (*J. Amer. Chem. Soc.*, 1908, **30**, 1478) artificially added to fat is shown to be quoted wrongly in Leach's "Food Inspection and Analysis." It does detect carotin, as Leach states, but does not distinguish between carotin in genuine butter and carotin prepared from carrots. This accords with Cornelison's own statement and with the fact now known that the colouring matters are identical. The relation between Martin's test for artificial pigments in fats and Moore's test for carotin artificially added to fats is also confused by Leach (*loc. cit.*). Martin's general test for artificial colouring matter (ANALYST, 1885, **10**, 163; 1887, **12**, 70) is undoubtedly useful for the preliminary detection of artificial pigments, but is not applicable to the detection of either natural or added carotin in fat. Moore's test (ANALYST, 1886, **11**, 163) is not alone specific for carotin added artificially, but is given equally by the carotin of natural fats. Carotin is not dissolved out of the fat in Moore's test, as he supposed, but merely decolorised by the ferric chloride added. The reaction is shown to be one of oxidation.

Although no known modification of Moore's test serves to distinguish between natural and added carotin in fats, as a means of detecting carotin it is very useful, and the following simplified procedure is recommended: The rendered melted fat (10 c.c.) is shaken with successive portions of Martin's reagent (15 parts 95 per cent. alcohol and 2 parts carbon disulphide) until no more colour is extracted. The extracted colouring matter is tested for annatto and other pigments by one or more of the approved methods. All the alcohol is drained off from the fat, and the pigment remaining in the fat is tested for carotin by adding a small crystal of pure ferric chloride to the hot melted fat. After thorough shaking, the fat is extracted with 10 c.c. of 95 per cent. alcohol. If the pigment was carotin, the fat which separates will, when melted, be seen to be completely decolorised. If only just sufficient ferric chloride be added to oxidise the carotin, the fat will be coloured green by the ferrous chloride, which is a product of the reaction (*cf.* Monier-Williams, ANALYST, 1912, **37**, 596). G. C. J.

Analysis of Saffron. Pierlot. (*Ann. Falsific.*, 1916, **9**, 24-29.)—Estimation of the amount of ash in saffron ought to be accompanied by a qualitative examination of the ash, since the proportions of ash in pure saffron may vary from 5 to 7·5 per cent. The salts of most frequent occurrence as adulterants are borax, potassium nitrate, sodium and magnesium sulphates, alum, and potassium tartrate. In one sample barium sulphate was present. The nitrogen varies within much smaller limits. In the case of forty samples of different quality and origin the extreme limits for nitrogen were 2·22 and 2·437 per cent. Apparently, the nitrogen is present in the form of a protein. Pure saffron contains no trace of nitrate, and only a small proportion of ammonia. Fresh samples examined contained 0·015 to 0·04 per cent. of ammonia, while very old samples contained 0·20 to 0·27 per cent. The presence of nitrates may be detected by treating the saffron with sulphuric acid. Pure samples give an indigo-blue coloration, changing rapidly to reddish-brown and then to black, whereas, when

a nitrate is present, a peach coloration, changing to light rose; is obtained. Nitric nitrogen is readily estimated by reducing the nitrate to ammonia in the usual way. For the estimation of organic nitrogen, the nitric nitrogen must first be eliminated. This may be done by treating 1·5 to 2 grms. of the saffron with 1·5 grms. of pure dry ferrous chloride and 15 c.c. of strong hydrochloric acid. C. A. M.

Analysis of Spices. C. Arragon. (*Ann. Falsific.*, 1915, **8**, 345-346.)—The following results were obtained on the analysis of various spices, the figures, except in the case of the water content, expressing grms. per 100 grms. of dry material:

	Water.	Ash.	Fat.*	Essential Oil.*	Protein.	Cellulose.	Reducing Substances, and Starch.
White pepper (Muntok) ...	10·6	0·96	8·41	2·19	14·0	6·36	64·2
,, ,, ,, ...	11·4	0·94	8·42	3·58	15·0	5·81	65·7
,, ,, (Singapore) ...	10·7	1·50	8·85	2·13	13·0	5·54	66·7
Black pepper (Batavia) ...	10·0	5·12	10·53	2·67	14·4	11·7	46·1
,, ,, (Java) ...	10·2	4·64	8·90	2·78	14·2	13·0	48·6
,, ,, (Tellicherri)	9·5	4·72	8·05	2·47	12·8	15·0	52·8
Long pepper...	7·5	5·08	7·4	3·0	12·6	7·7	51·6
Pimento (Jamaica)	11·3	4·43	6·3	4·84	6·9	23·0	22·5
Cinnamon (Ceylon)... ...	11·4	3·95	1·3	2·74	3·7	38·5	21·4
,, ...	9·3	4·66	0·9	3·1	4·7	35·6	21·7
,, ...	8·2	4·30	0·6	2·9	3·7	34·9	25·1
,, (China)	11·0	2·13	1·4	2·9	3·8	28·0	37·7
,, ,, ...	10·5	3·08	1·6	2·9	3·4	28·9	35·2
Nutmegs (Banda)	5·8	2·69	40·2	6·25	7·8	5·66	33·0
,, ,, ...	5·6	2·88	39·9	7·32	7·5	6·61	31·3
,, ,, ...	3·75	2·49	39·7	9·34	7·4	6·87	29·3
,, ,, ...	3·0	2·69	70·0	6·78	7·1	4·72	31·9
,, (Java)	7·7	2·26	40·1	7·45	7·7	6·28	39·2
Mace (Banda)	11·5	2·10	26·0	12·0	6·8	4·29	40·9
,, ,, ...	5·5	1·93	23·7	13·75	6·9	3·30	40·3
Cloves (Zanzibar)	8·5	6·35	8·4	21·1	5·9	14·4	16·2
,, ,, ...	7·2	6·17	8·0	19·3	5·6	15·6	16·1
Aniseed (Spain)	9·2	6·93	25·5	7·7	20·2	19·2	24·6
Cumin (Holland)	10·5	7·27	22·9	2·3	22·6	13·4	20·4
Coriander	9·2	7·01	20·6	2·2	14·2	24·7	21·2
Laurel leaves	4·0	4·29	7·7	4·3	7·0	26·6	22·5
Cardamom (Ceylon) ...	7·8	11·65	2·1	3·3	14·2	18·7	39·7
,, (Malabar) ...	9·3	4·60	1·8	6·3	11·7	13·2	58·3
Ginger (Japan)	5·5	5·42	4·8	1·8	6·3	5·0	67·1
,, (Bengal)	7·3	7·57	3·8	2·9	7·7	8·2	63·0
Star aniseed	3·3	3·14	4·9	8·9	4·8	29·1	13·3
Aniseed (Japan)	4·4	3·31	4·4	2·6	5·8	32·1	13·0
Galanga	6·7	3·74	5·6	1·7	2·3	21·4	42·4

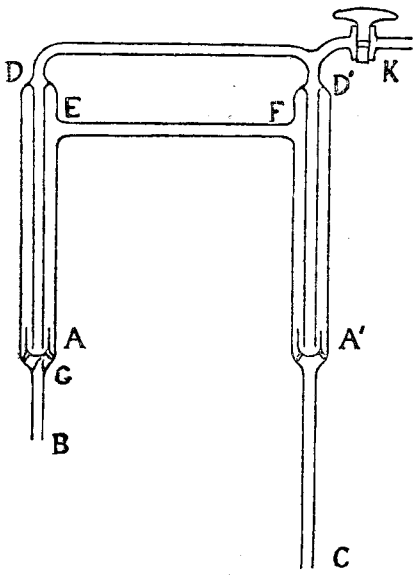
W. P. S.

* The essential oil and fat were estimated by weighing the ether extract and removing the former by distillation in steam.

Colorimetric Determination of Vanillin in Vanilla. T. von Fellenberg. (*Mitt. Lebensmitteluntersuch. Hyg.*, 1915, **6**, 267-274; through *J. Chem. Soc.*, 1916, **110**, ii., 355.)—One grm. of the finely divided sample is boiled under a reflux apparatus with four successive quantities of about 20 c.c. of water, the extracts are diluted to 100 c.c., 0·5 grm. of kieselguhr is added, and the mixture filtered. Fifty c.c. of the filtrate are extracted five times with alcohol-free ether, using 150 c.c. of the solvent altogether, the ethereal solution is treated with solid calcium chloride, filtered, evaporated to a small volume, and the remainder of the ether removed by a current of air. The residue is warmed to 60° C. with 30 c.c. of water, the solution filtered, and the filtrate diluted to 100 c.c.; 5 c.c. of this solution are then treated with 5 c.c. of 1 per cent. isobutyl alcohol solution (in 95 per cent. alcohol) and 20 c.c. of concentrated sulphuric acid, and the coloration produced is compared, after forty-five minutes, with that given by a known quantity of vanillin. It is recommended that the vanillin should be estimated separately in the outer and inner portions of the vanilla pod; in the case of normal vanilla, these two portions contain approximately the same quantity of vanillin, and a difference would indicate that some of the vanillin had been extracted from the outer portion.

BACTERIOLOGICAL, PHYSIOLOGICAL, ETC.

Chemical Composition of *Oscillaria Prolifica*. B. B. Turner. (*J. Amer. Chem. Soc.*, 1916, **38**, 1402-1417.)—The air-dried substance of this alga contains 46·25 per cent. of proteins, 9·70 per cent. of moisture, 6·40 per cent. of ash, and 2·20 per cent. of substances soluble in ether. The remaining 35·5 per cent. consists mainly of carbohydrates. A small quantity of a crystalline magnesium salt of an organic acid (possibly caproic) was obtained from the alga; saponin is not present in appreciable amount, but a glucoside or polysaccharide having physical properties similar to saponin exists in the plant. The bad smell and taste of the decaying alga appears to be due largely to higher acids of the fatty series. Indole and skatole are present in traces, as is also an aromatic compound which is soluble in petroleum spirit. The alga contains chlorophyll and a blue substance soluble in water and glycerol, the solutions having an intense red fluorescence. The chief carbohydrate in the plant is a pectin-like substance; this is hydrolysed very slowly by boiling with 5 per cent. sulphuric acid, the products being a non-reducing substance with a high positive rotation and a reducing sugar with a smaller rotatory power. A new form of extraction apparatus, suitable for continuous extraction of large quantities of material with volatile solvents, is



described. It consists of a double siphon, so constructed that an intermittent flow is obtained, as in a Soxhlet apparatus, allowing of the periodic filling and emptying automatically of an ordinary flask between two fixed levels without a tubulure or aperture in the side of the flask. This apparatus is shown in the illustration. The outer tubes must not be too wide, nor the inner tubes too narrow, as a large volume of air in the outer siphon delays the filling of the outer limb, *A' C*, whilst if the inner tubes are not wide enough to allow a fairly rapid flow of liquid from one cup to another, *A'* and *A*, the outer limb may not fill at all, and the liquid will trickle over, so that the level of the liquid in the flask cannot be drawn below that of the cups, *A'* and *A*. The tap, *K*, is introduced for convenience in filling. The sealed glass joints at *D* and *D'* may be replaced by corks, and the tube, *E F*, made in two parts and connected by a rubber joint. A micro-Kjeldahl apparatus is described for the determination of nitrogen in very small quantities (10 mgrms.) of substance.

W. P. S.

Volatile Oil of *Euthamia Caroliniana (L.) Greene*. G. A. Russell. (*J. Amer. Chem. Soc.*, 1916, **38**, 1398-1402.)—The plant *Euthamia Caroliniana Greene* grows abundantly in moist, sandy old fields near the coast in the Eastern United States, especially in Florida; it is rarely found on new land or in woods. The small yellow blossoms of the plant yield 0·69 per cent. of volatile oil, which has a yellow colour and a characteristic aromatic odour. The oil has a specific gravity of 0·8587, a refractive index of 1·4804, and a specific rotation of $-10·80°$ at 23° C. It consists essentially of dipentene with a trace of pinene and possibly a small amount of limonene. Free acids are absent, but a small quantity of combined acids, probably formic and acetic acids, are present. Esters are present to the extent of 2·10 per cent., calculated as $CH_3COOC_{10}H_{17}$; the alcohols amount to 7·01 per cent., of which 5·35 per cent. are free, and 1·66 per cent. combined. Aldehydic substances are also present. In addition, the oil contains about 10 per cent. of a compound or compounds having lævo-rotatory properties and a comparatively high specific gravity.

W. P. S.

Optimal Reaction for Pepsin. S. Okada. (*Biochem. J.*, 1916, **10**, 126-129.)—The solution employed had always the same salt concentration—about 0·16 N. Experimental evidence is adduced for the conclusion that the optional point for the action of pepsin is about $[H^{\cdot}] = 4 \times 10^{-2}$. Between $[H^{\cdot}] = 5·8 \times 10^{-2}$ and $1·7 \times 10^{-2}$ there is no considerable difference in the rate of hydrolysis.

H. F. E. H.

Optimal Conditions for the Proteoclastic Action of Taka-Diastase. S. Okada. (*Biochem. J.*, 1916, **10**, 130-136.)—Taka-diastase, although usually employed by reason of its amyloclastic activity, has been shown by Wolgemuth (*Biochem. Zeitsch.*, 1916, **39**, 324) to contain, weight for weight, 100 times as much proteoclastic enzyme as human or animal pancreatic juice, so that its value from the clinical point of view is probably greater in this respect than for its starch-splitting capacity. Using as substrate Witte peptone, the author gives experimental

evidence for his conclusion that the optimal reaction is at $[H^{\cdot}] = 8{\cdot}5 \times 10^{-6}$—that is to say a medium of slightly acid reaction is better than one of neutral or slightly alkaline nature. It was also found that the proteoclastic activity is considerably resistant to acid, and regains its activity after neutralisation if the acidity does not exceed that usually met with in the stomach of men and animals. H. F. E. H.

Seed Kernels of *Pseudo-phœnix Vinifera Beccari*. A. L. van Scherpenberg. (*Chem. Weekblad.*, 1916, **13**, 862-871.)—The kernels of the fruit of the Haitian palm, *Pseudo-phœnix vinifera*, are known as "Grains Cartiers." Extracted with ether, they yielded a greyish-brown fat, melting at 23° C., and having an unpleasant odour. They had the following composition: Fat, 13·85; water, 11·65; proteins, 5·26; ash, 6·15; soluble carbohydrates, 19·98; crude cellulose, 9·95; and undetermined substances, 33·16, per cent. The dried material contained 0·63 per cent. of an acid saponin, and 1·32 per cent. of neutral saponin. C. A. M.

New Salt of Uric Acid and its Application to the Analysis of Uric Acid and Phenol. J. L. Morris. (*J. Biol. Chem.*, 1916, **25**, 205-210; through *J. Soc. Chem. Ind.*, 1916, **35**, 866.)—Attempts to obtain a compound of zinc and uric acid in a pure state were unsuccessful, but there is strong evidence that zinc urate is formed when uric acid and a zinc salt are brought together under certain conditions. Uric acid may be precipitated completely from its solution by means of zinc as follows: The uric acid solution is acidified with acetic acid, an excess of 10 per cent. zinc acetate solution is added, and the mixture is then rendered alkaline to litmus by the addition of saturated sodium carbonate solution. If it is desired to determine the amount of uric acid present, the precipitate formed is collected on a filter, dissolved in acetic acid, the solution treated with a small amount of bismuth carbonate, boiled, and saturated with hydrogen sulphide. The mixed bismuth and zinc sulphides are separated by filtration, the filtrate is boiled to expel hydrogen sulphide, then concentrated to about 10 c.c., and the uric acid estimated colorimetrically by means of phosphotungstic acid. The method is useful for the removal of uric acid from urine previous to the determination of phenol. Four c.c. of the urine are treated with 1 c.c. of 10 per cent. zinc acetate solution and a quantity of acetic acid sufficient to dissolve the zinc phosphate formed; the mixture is then rendered just alkaline with saturated sodium carbonate solution, filtered, and the precipitate washed with about 10 c.c. of dilute sodium carbonate solution. The filtrate is boiled with the addition of about 0·5 grm. of calcium carbonate and 1 c.c. of 10 per cent. sodium oxalate solution, filtered, the filtrate acidified with oxalic acid, and the phenol determined colorimetrically.

ORGANIC ANALYSIS.

Rapid Method for Accurate Determination of Total Carbon in Soils. R. M. Salter. (*J. Ind. and Eng. Chem.*, 1916, **8**, 637-639.)—The author resorts to direct combustion, which with suitable apparatus, such as is figured in the paper, makes it possible to carry out a series of estimations at about twenty-five minute

intervals. The sample (2 grms.) is mixed with 2 or 3 grms. of " alundum " (40-mesh) and placed in an " alundum " boat in an electrically heated tube furnace maintained at a temperature of 925° to 950° C. The forward part of the tube contains a 5-inch length of granular copper oxide. An asbestos plug is pushed in behind the boat. Oxygen is passed through the tube at the rate of 750 to 1,000 c.c. in twenty minutes, which is sufficient time for complete combustion. The absorbing apparatus and the purifying train must, of course, be chosen to suit this high gas speed. The author purifies his oxygen with potash, and absorbs the carbon dioxide from the soil with soda lime. The gases leaving the furnace pass in succession over heated granular zinc, which arrests sulphur dioxide, chlorine, and acid fumes, and over phosphoric anhydride, and thence through the weighed Fleming soda-lime tube, which has an upper section containing phosphoric anhydride. Duplicate estimations agree within 0·7 mgrm. carbon dioxide, equivalent to 0·1 per cent. carbon on a 2 grm. sample.

G. C. J.

Ninhydrin Reaction with Amino-Acids and Ammonium Salts. V. J. Harding and F. H. S. Warneford. (*J. Biol. Chem.*, 1916, **25**, 319-335; through *J. Soc. Chem. Ind.*, 1916, **35**, 865.)—The ninhydrin (triketohydrindene hydrate) reaction with ammonium salts, first pointed out as a general one by Neuberg (*Biochem. Zeits.*, 1913, **56**, 500), takes place only in the presence of hydroxyl ions, and these hydrolyse triketohydrindene hydrate to phenylglyoxal-*o*-carboxylic acid. In the ninhydrin reaction with amino-acids (Ruhemann, *J. Chem. Soc.*, 1910, **107**, 2030; 1911, **109**, 798), it is probable that the amino-acid is decomposed into ammonia and the corresponding glyoxal, the latter acting as the reducing agent. Whilst the ninhydrin reaction is given by 1 per cent. solutions of the ammonium salts of weak acids, the reaction is obtained in the case of ammonium chloride and nitrate only when the solutions of the latter are nearly saturated. The blue coloration produced in the reaction is due to the formation of the ammonium salt of diketohydrindylidene-diketohydrindamine. This colouring matter shows a broad absorption band when examined in dilute solution, the band extending from the red to the green part of the spectrum and blocking out almost the whole of the yellow; the blue colour has a purple appearance when viewed in artificial light, and it is not oxidised by exposure to air.

Colorimetric Method for the Determination of Free Formaldehyde and Hexamethylenetetramine. R. J. Collins and P. J. Hanzlik. (*J. Biol. Chem.*, 1916, **25**, 231-237; through *J. Soc. Chem. Ind.*, 1916, **35**, 866.)—Aliquot portions of the formaldehyde solution are measured into Nessler tubes, 2 c.c. of phloroglucinol reagent (0·1 grm. of phloroglucinol dissolved in 10 c.c. of 10 per cent. sodium hydroxide solution) is added to each, and the mixtures are diluted to 50 c.c. After three minutes, the colorations obtained are compared with standard colours. The latter are prepared from definite quantities of Congo red solution (0·025 per cent. in water containing 5 per cent. of alcohol) and methyl orange solution (0·01 per cent. in water); 2·5 c.c. of the Congo red solution diluted to 50 c.c. gives the same coloration as 50 c.c. of 0·001 per cent. formaldehyde solution when both are viewed in a column

12 cm. in depth. Different samples of Congo red do not always give the same depth of colour, and the solution should be standardised against potassium bichromate; 2·5 c.c. of the 0·025 per cent. Congo red solution diluted to 50 c.c. should have the same tint as a mixture of 1·7616 grms. of potassium bichromate and 11·5537 grms. of sulphuric acid diluted to 50 c.c. The addition of methyl orange solution to the standards is necessary only when dealing with low concentrations of formaldehyde. The proportions of Congo red and methyl orange corresponding with different concentrations of formaldehyde are given in the following table, the mixtures being diluted to 50 c.c. and viewed in a 12 cm. column:

Formaldehyde.	Congo Red. (0·025 Per Cent. Solution.)	Methyl Orange. (0·01 Per Cent. Solution.)
Per Cent.	C.C.	C.C.
0·005	20·0	0
0·0033	11·0	0
0·0025	9·0	0
0·002	8·0	0
0·0016	5·0	0
0·00125	4·0	0
0·001	2·5	0
0·0005	0·85	0·4
0·0040	0·65	0·35
0·0002	0·23	0·18
0·00014	0·20	0·15
0·0001	0·13	0·10

To determine formaldehyde in urine, the phosphates present must be removed by treatment with sodium hydroxide solution and filtration before the above method is applied. Experiments with known quantities of formaldehyde showed that the method was more accurate than several other methods with which it was compared. The colorimetric method may be used to determine hexamethylenetetramine in urine, the latter being distilled without the addition of acid, and the process applied to the distillate. If formaldehyde is also present in the urine, this must be determined previously and its quantity deducted from the total amount.

Colour Reaction for "Oxycholesterol." M. C. Rosenheim. (*Biochem. J.*, 1916, **10**, 176-182.)—The author has shown (ANALYST, 1915, **40**, 129) that "oxycholesterol" when moistened with dimethyl sulphate gives immediately a characteristic purple colour, while no such colour is yielded by cholesterol, which, on the other hand, assumes gradually on warming a bright raspberry-red colour. The colour reaction of cholesterol with technical dimethyl sulphate has now been investigated, the spectrum showing two bands, from λ 560-λ 550 and from λ 500-λ 490. This reaction is not given by *pure* dimethyl sulphate, and appears to be due to the presence of monomethyl sulphate. The purple colour given with technical dimethyl sulphate and "oxycholesterol" shows an absorption band in the yellow

(λ 600-λ 580). Both *pure* and technical dimethyl sulphate, after the addition of an oxidising agent, such as ferric chloride, give a typical green colour reaction with "oxycholesterol," showing a well-defined absorption band in the red between λ 650 and λ 630. Cholesterol esters give the dimethyl sulphate reaction in a less degree, but vegetable cholesterols (phytosterols) behave exactly like cholesterol.

H. F. E. H.

Analysis of Proteins. I. Estimation of Arginine by Decomposition with Alkali. R. H. A. Plimmer. (*Biochem. J.*, 1916, **10**, 115-119.)—In the procedure suggested by Van Slyke (*J. Biol. Chem.*, 1911, **10**, 15) for the analysis of proteins, the arginine which is precipitated together with the histidine, lysine, and cystine, by phosphotungstic acid, is estimated by boiling the solution containing these four compounds with 50 per cent. caustic potash for six hours. Under these conditions the guanidine grouping of the arginine is decomposed, with the formation of ammonia, which is collected in excess of standard acid. Much difficulty was experienced in using this method, the strong alkali frequently causing the loss of the flask, and results being higher when copper vessels were employed. Varying times of boiling and concentrations of alkali were investigated, and the author finds that the estimation of arginine can be effected by boiling with 20 per cent. sodium hydroxide in place of 50 per cent. for six hours; the small loss of ammonia which occurs is counterbalanced by the slight decomposition of histidine which takes place when a solution of bases as obtained by Van Slyke's method is being analysed. The estimation cannot be effected in a copper flask if histidine is present, as under these conditions histidine undergoes considerable decomposition. It is advisable, on account of bumping due to solution of silica from the glass flask resulting in loss of nitrogen, to estimate the total nitrogen of the arginine and other bases in a fresh portion of the solution, and not in the residue from the arginine estimation. H. F. E. H.

Estimation of Reducing Sugars by Kendall's Solution, and the Construction of a Table indicating the Reducing Power of Lævulose. E. G. Wilson and W. R. G. Atkins. (*Biochem. J.*, 1916, **10**, 137-141.)—Kendall's solution (ANALYST, 1912, **37**, 205) consists of copper sulphate, potassium carbohate, and salicylic acid, and is free from many possibilities of error inherent in the use of Fehling's solution. Kendall (*loc. cit.*) gave values for dextrose, invert sugar, lactose, and maltose, and the authors have worked out a table connecting lævulose and weights of cupric oxide obtained when employing his method. An error of 0·001 grm. of cupric oxide corresponds to less than 0·0003 grm. lævulose, providing the weights employed are kept within the limits of the table appended. It is not permissible to employ 2 per cent. citric acid for the inversion of cane-sugar, if the resulting sugars are to be estimated by Kendall's solution, but invertase free from maltase must be used instead. The following expression was found to agree closely with the experimental results obtained, where y = weight of copper oxide (CuO), and x = weight of lævulose, both in grms.: $y = 0{\cdot}0006 + 3{\cdot}91x - 2{\cdot}601x^2$; but for accurate work the table given *in extenso* should be employed. H. F. E. H.

INORGANIC ANALYSIS.

Estimation of Aluminium as Oxide. W. Blum. (*J. Amer. Chem. Soc.*, 1916, **38**, 1282-1297.)—From observations made with a hydrogen electrode and with suitable indicators, it has been found that the precipitation of aluminium hydroxide by ammonium hydroxide is complete when $[H^+] = 10^{-6\cdot5}$ to $10^{-7\cdot5}$, points approximately defined by the colour change of methyl red and of rosolic acid. The presence of ammonium chloride during precipitation is advantageous in limiting the alkalinity and in coagulating the precipitate. Solutions of ammonium nitrate and chloride are equally satisfactory for washing the precipitate. Solutions should be heated to boiling, a few drops of 0·2 per cent. solution of methyl red added, and then ammonia drop by drop until the colour of the solution changes to a distinct yellow. After boiling for one or two minutes, filtration is proceeded with without delay. If the original solution does not contain a considerable amount of hydrochloric acid, at least 2·5 per cent. of ammonium chloride is dissolved in it before precipitation. Crucibles containing ignited alumina should be kept covered in desiccators and on the balance. In a large desiccator a small quantity of alumina contained in an uncovered crucible can readily absorb 1 per cent. of moisture from the air admitted to the desiccator when opening it for the reception of the crucible. Precipitates of 0·1 to 0·2 grm. alumina require to be blowpiped for at least five minutes, but ten minutes is always sufficient. The presence of ammonium chloride during ignition causes no appreciable loss of alumina. G. C. J.

Study of the Silver Arsenate Test for Arsenic. L. J. Curtman and P. Daschavsky. (*J. Amer. Chem. Soc.*, 1916, **38**, 1280-1282.)—With pure solutions of arsenate the test with silver nitrate is sensitive to 1 part in 150,000. In this concentration a faint brown coloration is given which can only be recognised readily by comparison with a blank. In a concentration of 1 part of arsenic (as arsenate) in 60,000 a decided and unmistakable precipitate is found. Ammonium nitrate, which is generally formed in carrying out the test, does not hinder the detection of arsenic in a concentration of 1 in 15,000. In systematic analysis the following procedure is recommended. The solution is neutralised with ammonia, about 12 per cent. of concentrated hydrochloric acid is added, the solution heated to boiling and treated with hydrogen sulphide. The solution is then diluted, so that the acid concentration is reduced to about 2·5 per cent., and treatment with hydrogen sulphide continued until precipitation is complete. The precipitate is collected on a filter, transferred to a beaker, heated for five minutes with 10 c.c. concentrated hydrochloric acid, and the solution is diluted and filtered. The residue, after washing free from chlorides with hot water, is transferred together with the filter to a dish, boiled with 2 c.c. nitric acid till nitrous fumes are no longer evolved, and the solution is diluted and filtered. The filtrate and washings are neutralised with ammonia, concentrated to 2 c.c. and mixed in a test-tube with 2 c.c. of 5 per cent. silver nitrate solution. The test will detect 0·5 mgrm. of arsenic with certainty. G. C. J.

Estimation of Calcium. E. Cahen and W. H. Hurtley. (*Biochem. J.*, 1916, **10**, 308-312.)—In the estimation of the calcium in aortas of normal and diseased persons, a calcined residue is often obtained which is only soluble with great difficulty in strong sulphuric acid, whereas it is readily soluble in phosphoric acid (1 vol. syrupy phosphoric acid and 3 vols. water). Such a solution can be used directly for the volumetric determination of the calcium as oxalate by decomposing with sulphuric acid, followed by permanganate titration; but if the calcium is to be determined gravimetrically the solution should be filtered after the solution of the calcium in phosphoric acid. It was found best to precipitate with oxalic acid, followed by ammonia, rather than to use ammonium oxalate, which gives a precipitate which is less crystalline, and filters badly. On applying the method to test mixtures of calcium and magnesium, experiments show that when the amount of magnesium as oxide exceeds the amount of calcium as oxide, a little of the former is precipitated along with the calcium. In such a case the precipitate of calcium oxalate is ignited, redissolved in a little phosphoric acid, and precipitated again. An excellent separation of calcium and barium sulphate may be made by taking advantage of the complete solubility of the former and insolubility of the latter in phosphoric acid. Calcium fluoride is also readily soluble in phosphoric acid.

H. F. E. H.

Modification of McCrudden's Method for Calcium, for Estimation of Calcium and Strontium in Presence of Phosphoric Acid and a Small Amount of Iron. O. B. Winter. (*J. Ind. and Eng. Chem.*, 1916, **8**, 603-604.)—McCrudden (*J. Biol. Chem.*, 1909, **7**, 83) precipitates calcium very slowly as oxalate in boiling solution containing a small amount of free hydrogen chloride. No soluble salts appear to be carried down by occlusion, and the method is excellent for calcium in foods, urine, and fæces, where much phosphoric acid and a little iron are always present. The method is not applicable to the estimation of strontium without modification, as strontium is not quantitatively precipitated under the above conditions. However, suitable addition of alcohol makes the precipitation of strontium complete without introducing any inconvenience. The solution to be analysed is diluted to 200 c.c., and made slightly alkaline with ammonia, using alizarin as indicator. It is then made just acid with $\frac{N}{2}$ hydrochloric acid, of which an excess of 10 c.c. is then added, together with 10 c.c. of 2·5 per cent. oxalic acid. The mixture is boiled until the precipitate is coarsely granular, and then ammonium oxalate solution, in amount about twice that necesssary to precipitate all the calcium and strontium, is added a few drops at a time with constant stirring. To the cooled solution 8 c.c. of 20 per cent. sodium acetate and 15 c.c. of alcohol are added, and the mixture allowed to stand overnight, or not less than four hours. The precipitate is filtered off and washed, first with 1 per cent. ammonium oxalate in 20 per cent. alcohol, and finally with a little 20 per cent. alcohol. The ignited oxides are dissolved in nitric acid, the solution evaporated to dryness, the calcium nitrate extracted with a mixture of absolute alcohol and ether, and calcium and strontium then each estimated in the usual manner.

G. C. J.

Separation and Estimation of Polysulphides and Thiosulphate in Lime-Sulphur Solutions. S. D. Averitt. (*J. Ind. and Eng. Chem.*, 1916, **8**, 623-627.)—The following method, due to J. E. Harris (Michigan Experiment Station, 1911, *Tech. Bull.* **6**), which is much the simplest method yet described for the purpose, has been submitted to experimental comparison with other methods of unquestionable accuracy, and found to be thoroughly trustworthy.

From 5 to 20 grms. of the sample, depending on its concentration, are diluted to 200 c.c. with freshly boiled and cooled distilled water, and transferred to small bottles, which are filled quite full and sealed. In routine work this sealing up is unnecessary, as the analysis may be completed immediately, but for the purpose of the author's experiments it was necessary to preserve the solutions, and sealed in this way they may be kept a long time unchanged. Ten c.c. of the dilution are run into a 200 c.c. conical flask with about 15 c.c. freshly boiled and cooled distilled water, and titrated immediately with $\frac{N}{10}$ iodine, until the yellow colour due to polysulphide becomes very faint. Up to this point the titration should be conducted rapidly with constant shaking to prevent a local concentration of iodine oxidising an appreciable amount of thiosulphate to tetrathionate. A very small crystal of sodium nitroprusside is next added, the solution shaken until the purple colour develops distinctly, and iodine solution added quickly but carefully until the colour is just discharged. The consumption of iodine up to this stage is the measure of the calcium present as sulphide. The titration is continued until 1 drop of undecomposed iodine solution imparts a faint colour to the liquid. The consumption of iodine during this second stage is the measure of the thiosulphate present.

The accuracy of the above method is shown by comparison with Thompson and Whittier's method (Delaware College Experiment Station, 1914, Bull. **105**) and with two new methods, the theoretical accuracy of which are unquestionable. As these latter methods, however, like Thompson and Whittier's, are tedious, and were only developed to test the method now recommended, they will not be described in this abstract.

Finally, to know the exact composition of lime-sulphur solution, which consists essentially of calcium polysulphide and thiosulphate, it is necessary to estimate the total sulphide sulphur. As this is all precipitated during the titration, and can be readily filtered after a few hours or at once after addition of 2 or 3 drops of hydrochloric acid and warming, all that is necessary is to filter it off on a tared filter of close texture. G. C. J.

Separation of Thorium from Iron with the Aid of the Ammonium Salt of Nitrosophenylhydroxylamine ("Cupferron"). W. M. Thornton jun. (*Chem. News*, 1916, **114**, 13-14.)—The ammonium salt of nitrosophenylhydroxylamine ("cupferron") was first introduced into analytical chemistry by Baudisch (ANALYST, 1910, **35**, 78), and affords a clean separation in the case of certain difficult mixtures. It affords a quantitative precipitation of titanium and an easy separation of that metal from aluminium. It precipitates titanium in presence of tartaric acid, so that after throwing down iron as ferrous sulphide, and acidifying, the titanium may be separated from aluminium and phosphoric acid. In a similar

manner " cupferron " may be used to precipitate zirconium, and for the separation of zirconium from iron and aluminium. In the present investigation the conditions for the quantitative precipitation of thorium have been studied. Contrary to the case of the cupferron compounds of titanium and zirconium, which are quantitatively precipitated in presence of free sulphuric acid, it is found that with the thorium compound the presence even of a small amount of free mineral acid prevents complete precipitation. In this case the mineral acid must be neutralised by the addition of ammonium acetate, so that precipitation takes place in presence of acetic acid. Twenty-five c.c. of a standard acidified solution of thorium sulphate, equivalent to 0·092 grm. of thorium oxide, were treated with 15 grms. of ammonium acetate and the volume made up to 500 c.c. A 5 per cent. solution of " cupferron " was then added gradually with constant stirring, 15 c.c. being used. The precipitate, being thoroughly coagulated by stirring, was collected on a filter, washed with a 1 per cent. solution of ammonium acetate, and dried on the paper at 100°-110° C. in a platinum crucible, then ignited to constant weight, using the blast lamp. The results for thorium oxide were within the ordinary limits of error for gravimetric work. The thorium salt of nitrosophenylhydroxylamine, $[C_6H_5(NO).N.O]_4Th$, differs somewhat from the titanium and zirconium salts. It resembles the latter in appearance, but, besides being sensibly soluble in presence of mineral acid, it differs in texture, so that it cannot be collected on a suction filter without appreciable loss. The separation of thorium from iron is effected by adding sufficient tartaric acid to hold up the bases in ammoniacal solution; the liquid is made slightly alkaline with ammonia, the iron precipitated by colourless ammonium sulphide, the filtrate boiled with a little sulphuric acid, and the thorium precipitated after the addition of 25 grms. of ammonium acetate in the manner described. It is not contended, however, that this method offers any general advantage over the well-known and satisfactory oxalate method for the estimation of thorium. J. F. B.

Qualitative and Quantitative Analysis of Tungsten. M. L. Hartman. (*Chem. News*, 1916, **114**, 27-28.)—The qualitative reduction test for tungsten is thus described: Boil at least 0·2 grm. of finely powdered material in a test-tube with concentrated hydrochloric acid until about half of the acid is evaporated. Dilute with an equal volume of water, add a piece of metallic tin, and heat if necessary. A fine blue colour in the solution, or a blue residue, indicates the presence of tungsten. If this test gives negative results, 0·5 grm. of the substance should be fused with 4 grms. of sodium carbonate, the melt dissolved in water, acidified with an equal volume of strong hydrochloric acid, treated with tin, and warmed if necessary. The volume of the solution should not exceed 10 to 20 c.c. In either case, if reduction is continued long enough, the blue colour is replaced by brown. These tests will show the presence of tungsten in materials containing 2 per cent., or, with special precautions, even less. Columbium (niobium) gives a blue colour under similar conditions, which disappears on dilution. Vanadium gives a blue colour in reduced solutions, but tartaric acid will cause this reduction, whereas it will not reduce tungstic oxide. Molybdenum goes through a series of colour changes from violet to blue or black. Titanium gives a violet colour. Three alternative methods for the

quantitative estimation of tungsten are given. The hydrofluoric acid method and the alkali fusion method are quoted from A. H. Low's "Technical Methods of Ore Analysis." It may be necessary to purify the tungstic oxide from co-precipitated stannic oxide by volatilisation of the stannic oxide in the form of stannic chloride on heating with ammonium chloride. To do this effectively, the crucible containing the mixed oxides and ammonium chloride should be placed inside a larger one with a cover, and the whole ignited with the cover on until the chloride is completely volatilised. Ignition in absence of air darkens the colour of the tungstic oxide, and the inner crucible should then be ignited with full access of air until the pure yellow colour is restored. The operations are repeated until the weight becomes constant. Another method for the estimation of tungsten in ores, preferred by some chemists, is the aqua regia method. One grm. of the finely powdered ore is digested below the boiling-point with 50 c.c. of aqua regia. When the solution has evaporated to 10 to 15 c.c., it is diluted with 50 c.c. of hot water and allowed to stand for half an hour. It is decanted through a filter, and the residue washed several times by decantation with 50 c.c. of hot water each time. The wash water should be slightly acidified with hydrochloric acid. The residue is treated with 20 c.c. of dilute ammonia, prepared by mixing 200 c.c. of strong ammonia solution with 1,000 c.c. of water and adding 10 c.c. of hydrochloric acid to form a little ammonium chloride. This dissolves the yellow tungstic oxide, and the solution is also decanted through the filter. When the residue is finally extracted and washed, the silica should be white. The tungstic oxide is recovered by evaporating the filtrate, igniting to expel the ammonium salts, and heating with hydrofluoric acid to free the residue from silica.

J. F. B.

Estimation of Vanadic Acid after Reduction by Metallic Silver. G. Edgar. (*J. Amer. Chem. Soc.*, 1916, **38**, 1297-1302.)—Vanadium is quantitatively reduced from the pentavalent to the tetravalent condition by metallic silver in acid solution under proper conditions. The reaction may be used to estimate vanadium (*a*) gravimetrically, from the loss in weight of the silver; (*b*) oxidimetrically, by titration with permanganate; or (*c*) by titration of the dissolved silver with thiocyanate. All these operations may be carried out on the same solution and serve to check each other.

Solutions of sodium vanadate are acidified with 2 c.c. of sulphuric acid, dilated to about 75 c.c., and treated with a known weight (1-2 grms.) of silver reduced by zinc, silver prepared by heating the oxide, or preferably, perhaps, by electrolytic silver, as this is more apt to be pure. The solutions are boiled for twenty to thirty minutes, or for ten minutes after the appearance of a pure blue colour. They are then filtered through porcelain Gooch crucibles, and the silver washed with hot water. The crucibles are placed in larger nickel crucibles and heated with the full flame of a large Bunsen burner for thirty minutes. From the loss in weight of the silver the vanadic acid can be calculated. The filtrate from the silver can, alternatively or in addition to the gravimetric estimation, be titrated hot with $\frac{N}{20}$ permanganate, and at the completion of this titration the silver in the cooled solution can be titrated with $\frac{N}{20}$ ammonium thiocyanate, using ferric alum as indicator. The

volumetric modifications are as exact as the gravimetric, and serve to estimate 0·13 grm. of vanadic acid with an error not exceeding 0·4 mgrm. G. C. J.

APPARATUS, ETC.

Temperature Effect in Dialysis, and a Simple Rapid Dialyser. M. Neidle. (*J. Amer. Chem. Soc.*, 1916, **38**, 1270-1272.)—Large quantities of inorganic hydrosols, containing only minute amounts of electrolytes, may be prepared in a comparatively short time if the difference in concentration of diffusible substances in the internal and external liquids is large, and if the temperature of the two liquids is raised. To obtain this acceleration in the process, the author suspends a parchment paper membrane container of about 1 litre capacity in a 2-litre beaker containing about 1 litre of the solution to be dialysed. Distilled water is run at a fairly constant rate into the membrane, which is maintained a little more than half full by means of an automatic siphon. The colloidal solution in the beaker is heated to 70°-90° C. by a burner placed under the beaker. This apparatus will give in twenty days a hydrated ferric oxide hydrosol as pure as if not purer than the same hydrosol prepared by dialysis in the cold for six months; a colloidal solution, satisfactory for most purposes, may be prepared in eight to ten days, whilst the usual method requires about one month.

W. P. S.

REVIEW.

LIGHT AND COLOUR THEORIES. By JOSEPH W. LOVIBOND. London: E. and F. N. Spon, 1915. Price 6s. net.

To the author of this little book the scientific workers of a number of different industries are indebted for a simple instrument, the tintometer, allowing of the rapid and exact measurement of the depth of colour of the materials with which these industries deal. The numerical results furnished by the Lovibond tintometer are expressed, it is true, in arbitrary units, but they have none the less proved of great practical value. The series of coloured glasses supplied with the instrument appear to have been standardised with extreme care, and no instance of complaint in this direction is known to the writer, who has had considerable experience of the tintometer in its application to the examination of brewing materials.

In the light of these undoubted facts, a work treating of the practical and theoretical evolution of the tintometer promises well. That the fulfilment corresponds in any way with the anticipation is, unfortunately, not the case, the sequence and clearness so peculiarly necessary to a subject of this character being conspicuously absent. From the experimental data obtained by the author, the latter deduces a theory which is summed up in a code of nine governing laws. The first of these laws reads: "Normal white light is made up of the six colour rays—red, orange, yellow, green, blue, and violet—in equal proportions. When the rays are in

unequal proportions the light is abnormal and coloured." No explanation is given of the meaning of the expression, "equal proportions," and the obscurity is by no means lessened by the inadequate chapter headed "Evolution of the Unit," which contains the sentence: "This suggested the idea that if the three colours [red, yellow, and blue] could be so balanced that the light transmitted was colourless, it would be evidence of equivalence of intensity in the individual colours." Exactly what is meant by the statement that "the vision can separate six monochromatic colours from a beam of white light" (p. 17) is a matter for conjecture. Similar examples are only too numerous.

That trouble has been expended in the preparation of the book cannot be denied, but the insertion of diagrams coloured by hand does not compensate for lack of accuracy, looseness of expression, and other glaring faults.

The book closes with an appendix in which Dr. Dudley Corbett describes a method of X-ray dosage by means of the Lovibond tintometer.

T. H. Pope.