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Barium as a Normal Constituent of Brazil Nuts

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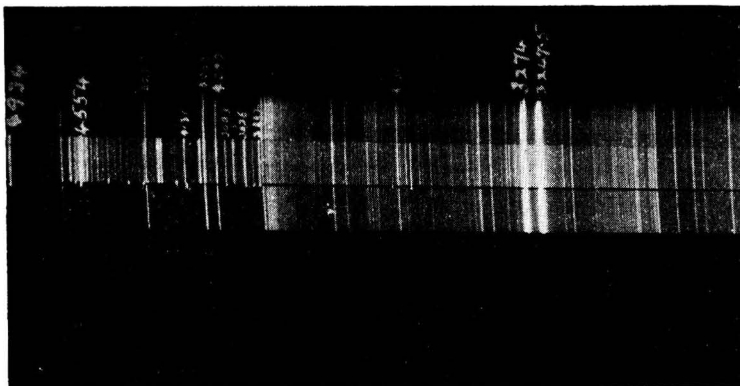
(*Read at the Meeting, May,* 1933)

About a year ago a sample of mixed sweets was submitted with the request that they should be examined for the presence of anything likely to cause sickness.

During the examination for metallic poisons a yellow precipitate was obtained with potassium chromate, and at first the presence of lead was suspected; but,



Ultra-violet spectrograph of ash of Brazil nut kernels, taken on copper electrodes as shown in the centre band, where most of the barium lines are indicated by dots. The outside bands represent the spectrum of the electrodes.

on further investigation, the precipitate was found to be due to the presence of barium. The absence of lead and the presence of barium were subsequently confirmed by ultra-violet spectrographs. (See illustration.)

It was necessary, therefore, to ascertain the source of the barium. The sweets were fondants of various colours. Some contained almonds, some walnuts,

and others Brazil nuts, though it was some time before any suspicion was directed to the nuts. The sugar, the various colours, and the flavours were examined with negative results; but, finally, the nuts were separately examined, and it was found that the barium came from the Brazil nuts. It was thought at first that it might be due to some treatment of the outside of the kernels, and outside and inside portions were separately examined; barium was found in each case. It seemed probable, therefore, that the barium was a natural constituent of the nuts. This was confirmed by obtaining several samples of unshelled nuts from various sources. In every case barium was found.

The percentage of barium in the nuts used in the sweets, calculated as metallic barium, amounted to 0·29. Further, an attempt was made to determine whether any water-soluble barium was present. A trace was found in this sample and in one other, but usually no trace of water-soluble barium seems to be present in Brazil nuts.

In view of these findings our clients were informed that there was no evidence of any contamination of the sweets, and that the trouble was probably due to idiosyncrasy of the persons concerned. This conclusion was supported by the fact that apparently only a single complaint was made concerning the sweets.

I was not able to go further into this question at that time, but recently I have determined the barium in a considerable number of Brazil nuts from different supplies, including some from the Manaos and some from the Para districts of Brazil, and the nuts tested cover two seasons' supplies. (See Table.)

Nut	Barium Per Cent.	Nut	Barium Per Cent.
1. From sweets, probably Manaos	0·29	10. Probably Manaos	0·22
2. Unknown, probably Manaos..	0·19	11. Para	0·07
3. Unknown, probably Manaos..	0·10	12. Para	0·02
4. Manaos	0·18	13. Para	0·17
5. Manaos	0·21	14. Para	0·09
6. Manaos	0·25	15. Unknown.. ..	0·29
7. Manaos	0·15	16. Unknown.. ..	0·06
8. Manaos	0·25	17. Unknown.. ..	0·11
9. Unknown, probably Manaos..	0·31		

In every instance I have found barium, but only in two (Nos. 9 and 15) was the percentage so high as that obtained in the nuts taken from the sweets. It may be noted that, as a rule, the Para nuts give smaller percentages.

The procedure adopted for the determination of the barium was as follows: Fifty grms. of the kernels were ashed at a low temperature. The ash was treated with hot dilute hydrochloric acid (containing about 5 per cent. of acid of sp.gr. 1·16). A little dilute sulphuric acid was added, and the whole was allowed to stand for at least an hour. The residue and precipitate were filtered off, washed, ignited and fused with fusion mixture ($3Na_2CO_3 + 2K_2CO_3$). The fused mass was digested with water containing about 3 c.c. of ammonia (sp.gr. 0·880) per 100 c.c., and, when it was thoroughly disintegrated, a precipitate (mainly barium carbonate) settled. This was filtered off, washed free from sulphates with water containing a little ammonia, and treated with hot dilute acetic acid. The filtrate was evaporated until practically the whole of the acetic acid had been driven

off. Water was added, and, finally, ammonium chromate solution. The whole was boiled and then allowed to stand overnight. The barium chromate was filtered off on a Gooch crucible, washed with cold water, and dried in the water-oven.

This procedure was tested upon a sample of pure barium sulphate that had been obtained by fusing a fairly pure sample with fusion mixture, taking the mass up with water, dissolving the residue in acetic acid, precipitating with ammonium chromate, dissolving the precipitate in dilute hydrochloric acid, precipitating with dilute sulphuric acid, filtering off the precipitate, dissolving it in concentrated sulphuric acid, and finally precipitating the barium sulphate with water and washing it free from chlorides, etc. Of this purified barium sulphate, 0·3845 grm. was taken (equivalent to 0·2263 grm. of Ba). When this was treated by the procedure used in the analysis of the nut ashes, 0·4180 grm. (equivalent to 0·2265 grm. of Ba) of barium chromate was obtained.

The following are illustrations of the effect of cold water, etc., on barium chromate contained in Gooch crucibles, and previously washed with cold water:

			Grm.
A.	(i)	Original weight	0·0845
	(ii)	After 100 c.c. of cold water	0·0845
	(iii)	After 100 c.c. of hot water	0·0830
	(iv)	After 100 c.c. of 5 per cent. hot ammonium acetate solution, followed by cold water	0·0770
	(v)	After 100 c.c. of approx. 3 per cent. acetic acid (by vol.)	0·0760
B.	(i)	Original weight	0·1375
	(ii)	After 100 c.c. of cold water	0·1370
	(iii)	After 100 c.c. of cold 6 per cent. ammonium acetate solution	0·1355
	(iv)	After 100 c.c. of 3 per cent. acetic acid (by vol.) ..	0·1335

The determination as chromate was thought desirable in order to ensure separation from calcium, but probably approximate determinations of the barium could be obtained by direct precipitation with sulphuric acid in the presence of sufficient dilute hydrochloric acid.

Some work was also done in order to throw light upon the state of combination of the barium.

A sample of nuts containing 0·18 per cent. of barium was calcined, and the ash was treated with dilute hydrochloric acid and filtered off without the addition of sulphuric acid. The residue on the filter, when ignited and weighed, amounted to 0·04 per cent., calculated on the nut kernel. It was then fused with fusion mixture and the barium was determined in the usual way as chromate. The chromate obtained was equivalent to 0·018 per cent. of barium (= 0·031 per cent. $BaSO_4$). Another portion was ashed, and the ash was treated with hydrogen peroxide to oxidise any sulphide to sulphate. It was then treated with dilute hydrochloric acid, filtered off, washed and weighed. Its weight amounted to 0·07 per cent., calculated on the kernel. The difference between this and the previous result, *viz.* 0·03 per cent., probably represents barium sulphate which had been reduced during the ashing; therefore, the total barium sulphate that could be formed is 0·031 + 0·030 = 0·061 per cent. = 0·036 per cent. of barium. This, of course,

may not have been present as such in the kernel itself, but may have been formed by decomposition of organic sulphur compounds on ignition. In any case there was in these kernels at least 0·18 — 0·036 = 0·144 per cent. of barium combined with some radicle other than SO_4, and which, therefore, might be solubilised under certain conditions.

There was not sufficient of this sample to go any further, but another containing 0·15 per cent. of barium in the kernels was taken. Fifty grms. of this were extracted (i) with ether, (ii) with industrial methylated spirit, (iii) with water, (iv) with dilute hydrochloric acid containing 5 c.c. of acid of sp. gr. 1·16 per 100 c.c. (=1·58 per cent. of HCl). A very slight trace of barium was obtained from the ethereal extract, but nothing from the alcohol and water extracts. The dilute hydrochloric acid extract was obtained by allowing the portion that had been treated with ether, alcohol and water to soak for some hours in 100 c.c. of the acid. It was then filtered off on a Buchner funnel and washed with 50 c.c. of the same dilute acid. The filtrate was found to contain an amount of barium equivalent to 0·116 per cent. of barium calculated on the original kernels.

Experiments were then carried out to find the effect of weaker acid upon the original kernels as follows: Twenty-five grms., after grating, were allowed to soak overnight in 100 c.c. of 0·15 per cent. hydrochloric acid (w/w). The mass was then filtered off on a Buchner funnel and washed with 50 c.c. of 0·15 per cent. hydrochloric acid. From the filtrate an amount of barium equivalent to 0·08 per cent., calculated on the kernels, was obtained. Twenty-five grms. of kernels soaked in 50 c.c. of 0·02 per cent. hydrochloric acid gave no indication of barium in the filtrate, whilst 25 grms. in 50 c.c. of 0·046 per cent. hydrochloric acid gave a trace of barium, but probably not more than 0·002 per cent.

From this it appears that very low concentrations of hydrochloric acid have little effect in solubilising the barium; but with a concentration of 0·15 per cent. a fair proportion of barium goes into solution, and, with higher concentration, probably almost the whole of the barium dissolves. This suggests that the normal concentration of hydrochloric acid in the human stomach (0·35 to 0·45 per cent.) may be capable of solubilising barium, and in cases where the concentration is above the normal there will be a greater tendency for the barium to dissolve.

The effect of lactic acid was then tried by treating 50 grms. of grated nuts with 100 c.c. of water to which 1 c.c. of 44 per cent. lactic acid had been added. The amount of barium in solution was found to be equivalent to 0·023 grm. of the metal. It was found also that 5 per cent. acetic acid had a strong solvent action and that small quantities were dissolved by 1 per cent. acetic acid.

It seems possible that the barium exists in the nuts as a salt of an organic acid, and that this salt is insoluble in water but soluble in acids. Some attempt was made to separate and isolate the acid by treating the nuts with dilute acetic acid, to extract the barium salt, and adding an amount of sulphuric acid equivalent to the barium present, in the hope that the acid with which the barium is supposed to be combined is soluble in water and could be isolated from the filtrate obtained by filtering off the barium sulphate. Great difficulties were encountered, however, from the presence of soluble protein which came out continuously during concentration. Also, it was found that on merely boiling the acetic acid solution before

adding sulphuric acid, precipitates were obtained which contained appreciable quantities of barium.

Incidentally, it may be noted that if the maximum medicinal dose of barium chloride ($BaCl_2 \cdot 2H_2O$) is 2 grains (as given in Hale White's *Materia Medica*), only about eight nuts of average size would be required to correspond with this, assuming all the barium to be solubilised. Although one can hardly suppose that with the average person the barium in Brazil nuts has any harmful effect, yet I have heard of people upon whom the nuts produce symptoms that suggest those produced by soluble barium salts, and it may be that in these persons the barium is easily solubilised. In any case, it is interesting that the barium salt is freely solubilised by 0·15 per cent. hydrochloric acid, and it is noteworthy that the percentage of barium in the sweets mentioned at the beginning of this paper is higher than is usually found in Brazil nuts.

The occurrence of barium in Brazil nuts suggests that the soil in which they grow must contain appreciable quantities of that element, and the question arises whether any other Brazilian products contain barium. In this connection I tested some Brazil oranges with negative results, and some Brazil sugars, in which I found a slight trace, but the amount from 25 grms. was unweighable on an ordinary balance.

Since the above work was done I have found that the sensitive test for barium, by means of the sodium salt of rhodizonic acid, described by Feigl in *Mikrochemie*, 1924, p. 188, and in the *B.D.H. Reagents for Spot Tests*,* can be applied directly to the cut kernels of Brazil nuts, and the presence of the element is shown very clearly. A weak solution of the reagent in water (say 0·5 to 1 per cent.) is spotted on to the surface of the kernel and left for a short while. A drop or two of $N/10$ hydrochloric acid is then added. If no barium is present the orange colour of the reagent disappears on the addition of the acid (after a preliminary darkening), whilst in the presence of barium a brownish-red colour remains. Almonds treated in this way gave negative results, but almonds which had been soaked in 0·05 per cent. barium chloride solution gave a strong reaction. Although not absolutely necessary, it is preferable to soak the kernels for some time in ether in order to remove the outer portions of the oil to allow the reagent to penetrate better.

In conclusion, I should like to thank those members of our laboratory staff who have helped me with this investigation.

Discussion

The PRESIDENT said that he had never suspected the presence of barium in nuts or other vegetable products. It was possible that this element had been overlooked, and that its presence might be of some significance.

Mr. A. L. BACHARACH suggested that the author might investigate the effect of synthetic gastric juice on the nuts, for, although the hydrochloric acid in the gastric juice would dissolve barium, there were other ions present that would tend to precipitate the barium in an insoluble form.

Mr. SEABER, replying, said that he had cut away the brown skin of the nuts and had used only the white kernels in his tests. Referring to the suggestion

* Published by the British Drug Houses Ltd., Graham Street, City Road, London, N.1.

that the toxic symptoms sometimes produced by Brazil nuts might be due to the presence of cyanogen, he said that he was not aware that cyanogen had been found in Brazil nuts. He did not wish to assert that the barium in the nuts had a bad effect; it merely happened that in this case there was some sickness. He had not gone deeply into the question of the general effect of barium, or whether the barium in Brazil nuts became soluble in the stomach, and he had merely suggested possible explanations. It would be very interesting to determine to what extent the barium did dissolve.

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The Determination of Graphitic Silicon in a Siliceous Residue

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In previous papers (Analyst, 1932, **57**, 500; 1933, 81) methods have been given for the determination of total silicon in aluminium, and the effect of heat treatment of the metal on the results obtained by the mixed acid method of estimation has been shown. The influence of *variations* in the proportion of silicon in solid solution, for the same total silicon on the electrical, mechanical, and physical properties of the commercial metal has also been pointed out. It is therefore important to have a quantitative method for estimating these variations, but up to the present no convenient and accurate method has been available.

Several workers have studied and published methods which are stated to determine the silicon in the siliceous residue from acid attack on aluminium, the figures so obtained being supposed to correspond with the amount of free or graphitic silicon in the metal. Rosenhain has drawn attention to this supposed quantitative relation in the following words (*J. Inst. Metals*, 1917, **2**, 167): "When aluminium was dissolved in *aqua regia*, the free silicon which occurs in particles of moderate size resisted oxidation to a very considerable extent, and remained as a dark insoluble residue which the analyst reported as silicon. The silicon in solid solution, when the aluminium dissolved, was left exposed to the strongly oxidising nitric acid in a state of extremely fine division, and possibly in a different allotropic modification from the free silicon, with the result that it became oxidised and was returned in the analysis as silica." The above method for determining graphitic silicon, and most of the others which have been put forward (details of some of these methods can be found from the references given below)* are gravimetric, and depend on weighing the siliceous residue after various treatments. It is not proposed to go into these methods here, as a cursory examination shows that they are at best purely empirical, and the results which they give cannot correspond, except fortuitously, with the amount of silicon in the siliceous residue, or necessarily bear any relation to the

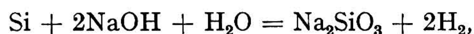
* von Prettner, *Chem.-Ztg.*, 1927, 261; Koster and Muller, *Z. Metallkunde*, 1927, 52; Hunt, Clapp and Handy, *J. Anal. Appl. Chem.*, Vol. 6, No. 1; F. Regelsberger, *Z. angew. Chem.*, 1891, 363, 442.

precipitation of silicon in the metal itself (*cf.* B. Ottani, *J. Inst. Metals*, 1926, **44**, 245).

It was thought, therefore, that it would be of more value to work out a process which actually determined the silicon in the residue. As it seems that with gravimetric processes the results must be empirical, owing to the variable combined water error, the oxidation during drying of the silicon in the residue and the solubility of silicon in hydrofluoric acid when that acid is used (C. Bedel, *Compt. rend.*, 1929, **189**, 180), it was decided to abandon altogether the idea of using a gravimetric process and to work out a method for the determination of silicon in the siliceous residue, which, by avoiding the weighing of this residue, would overcome all the difficulties of the gravimetric processes.

Gas-Volumetric Estimation of Silicon in Siliceous Residues.—Gas-volumetric methods do not appear to have been tried in connection with silicon in aluminium, although such methods are capable of a high degree of accuracy. For example, what are possibly the best early determinations of the atomic weight of aluminium were carried out by J. W. Mallet, using a gas-volumetric method. Mallet (*Trans. Roy. Soc.*, 1880, 1003) spent 23 years in investigating methods for this determination, and came to the conclusion that the most consistent and trustworthy method for determinations of the highest accuracy was undoubtedly the gas-volumetric one; his figures, although published 50 years ago, are in close agreement with the International atomic weight accepted to-day.

It seemed, therefore, that a gas-volumetric method might satisfactorily be used for the determination of silicon in silica residues, since silicon readily evolves hydrogen with caustic soda. Philips (*Z. angew. Chem.*, 1905, **14**, 1969) appears to have used previously such a method for silicon, with the object of determining the oxide-content without, however, giving any convincing results as to its accuracy or otherwise. The probable theoretical reaction is as follows:



$$Si + 2NaOH + H_2O = Na_2SiO_3 + 2H_2,$$

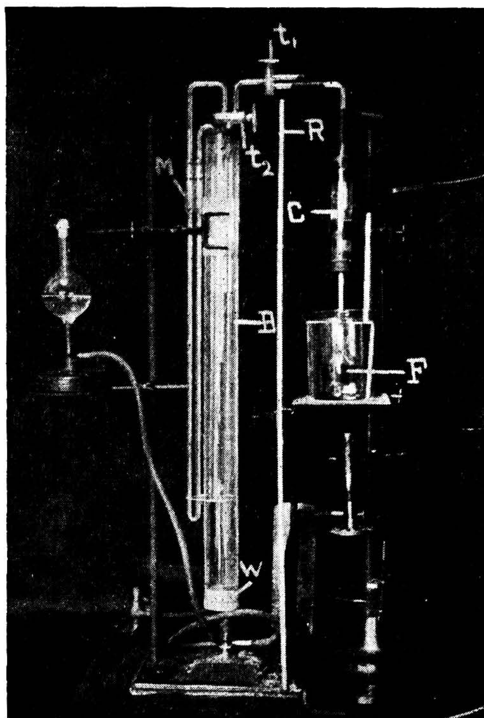
whence 0·0001 grm. of silicon $\equiv$ 0·16 c.c. of hydrogen at S.T.P.

Thus the theoretical possible accuracy of the method is certainly greater than the accuracy of weighing with the ordinary laboratory chemical balance. A further immense advantage in using a gasometric method for the purpose is that it avoids altogether the troublesome washing, drying and weighing of the silicon-silica mixture, which operations are the cause of all the trouble in the gravimetric method; for the gasometric method, only the original metal is weighed out.

Apparatus.—The apparatus used was a modified Hempel gas-volumeter fitted with a pressure-temperature compensator. The modifications consisted in an extension of the usual 100 c.c. burette by a bulb to allow for expansion on boiling; an arrangement for circulating cold water round the outside of the compensator and burette to ensure that both were always at the same temperature throughout their whole length; an additional three-way tap sealed on to the burette to allow the gases to be analysed at any period of an experiment; and, most important for accuracy, the introduction of a condenser between the reaction flask and the burette.

The apparatus is shown in the accompanying figure.

PROCEDURE.—Forty c.c. of 40 per cent. caustic soda solution are measured into the flask F, which is connected with the condenser and then immersed in a bath of water at room temperature, and left for about 15 minutes connected with the burette, the liquid in the burette being brought to about the zero mark, and the tap, t_2, being left open to the flask.



At the outset the temperature, T, of the water surrounding the flask is taken and the atmospheric pressure noted. The cooling bath is removed, the burette liquid adjusted to the zero, tap t_2 closed and tap t_1 temporarily removed from its socket, while the weighed material is wrapped in a small filter paper and introduced into the flask, which is then re-connected with the condenser. The tap t_1 is now replaced and connected with the burette, and the tap t_2 opened to connect with the flask. (It is found that there is always plenty of time to make these connections, as the reaction takes from 1 to 15 minutes to start in the cold.) The flask and its contents are then slowly heated just short of boiling; the silicon rapidly dissolves, tending to sink to the bottom of the liquid, whilst the filter paper floats on the top, tending to prevent spurting losses; when the silicon is nearly all dissolved the liquid is boiled for two periods of 1 minute each, when the action will be found to be complete unless the material is very coarse. (With finely divided silicon, such as is obtained from the metal, the reaction is completed below the boiling point in a very much shorter time than with the crystalline material). After boiling, the flask is immersed in a large cooling-bath (the temperature of this

bath being adjusted so that after completely cooling the flask the water will be at practically the same temperature as at the beginning of the experiment) and left for 20 to 30 minutes. During the whole course of the experiment and during the cooling, water at room temperature is circulated through the burette water-jacket and the condenser.

At the end of the determination the gas in the burette is adjusted to atmospheric pressure by means of the reservoir, the flask is cut off by closing the tap t_1, the tap t_2 is connected with the compensator manometer, and the column of gas in the burette is read, and corrected to S.T.P. From this volume of gas the equivalent weight of silicon is calculated.

ERRORS AND CORRECTIONS IN METHODS.—(1) *Loss of Liquid from Flask.*— Finely divided silicon readily dissolves in 10 per cent. sodium hydroxide solution, but in making determinations with this strength of soda on the crystalline material it was found that (before the condenser was included in the apparatus) the solution distilled into the burette, making the results as much as 3 or 4 per cent. too low.

By using 40 per cent. sodium hydroxide solution this loss was reduced to 0·3 per cent., determined by actual weighing of the flask and contents before and after the experiment. When a condenser was inserted between the flask and the burette, the amount of liquid carried over by the gas became negligible; actual weighings showed that it was not greater, for a single experiment, than 0·02 to 0·03 grm., and this was confirmed by numerous blank determinations in which the contraction of the burette liquid up the barrel of the tap was measured; these blanks gave figures of + 0·01 to − 0·02 c.c.

(2) *Loss of Reacting Solid from Flask.*—To test whether the loss of reacting solid from the flask was appreciable, the apparatus was first cleaned out completely and filled with fresh dilute sulphuric acid. Eight lots of siliceous residues containing various amounts of silicon were obtained by dissolving various samples of aluminium metal in hydrochloric acid and filtering off the siliceous residues on asbestos in Gooch filters; they were then successively analysed in the apparatus in the usual way. After each analysis the condenser tube was washed down with acid from the burette, and this acid was collected in a beaker. The 8 samples of acid were then examined against a white background for brown silicon, but no dark particles were visible in any sample. The acid was then heated until fumes appeared and the silica determined in the usual way. The results of these tests are given in Table I below.

TABLE I

TESTS FOR LOSS OF SILICON IN CONNECTING TUBES OF APPARATUS

Exp.	Metal	Graphitic silicon in residue by gasometric analysis Per Cent.	Weight of residue from fuming acid Grm.
414	Wire A	0·054	0·0005
415	,, ,, ...	0·052	0·0005
416	,, B	0·220	0·0005
417	,, ,, ...	0·215	0·0004
418	,, A	0·053	0·0005
419	Virgin 99·8 per cent. ingot ..	Nil	0·0004
420	Wire A	0·054	0·0005
421	Virgin 99·8 per cent. ingot ..	Nil	0·0003

The liquid in the flask for the experiments of Table I contains at least as much asbestos from the filter (average weight of dry pad about 0·4 grm.) as there is siliceous residue, and it may be assumed that this accounts for the relatively high losses obtained from the virgin ingot metal. Taking this metal as a blank, it will be found that the maximum loss from the siliceous residue amounts to 0·0002 grm. Assuming the siliceous residues to contain about 50 per cent. of silicon, the maximum loss of silicon would be 0·0001 grm. Since, however, no silicon particles were visible in any of the residues, it appears that any silicon carried out of the flask is either washed back again by water from the condensed steam or converted to silica by soda splashings from the flask. Any silicon converted into silica will evolve its equivalent amount of hydrogen, and will not therefore affect the results. From this the conclusion may be drawn that errors due to loss of reacting solid from the flask are likely to be negligible.

(3) *Temperature-Pressure Corrections.*—For accurate results it is advantageous to bring the reaction flask to room temperature at the beginning and end of the determination; the volume of air in the flask and connecting tubes is then very simply cut out by closing the tap t_1. In practice, however, it is found more convenient to use a measured volume of liquid in the flask and to determine, once for

TABLE II

EXPERIMENT SHOWING ACCURACY OF TEMPERATURE PRESSURE CORRECTIONS

	Volume against compensator c.c.	Temperature ° C.	Pressure Mm.
First reading of burette after cooling 25 minutes ..	88·7	24·3	768
Left overnight 16 hours	88·7	18·8	764
Connected to flask and then re-connected with compensator	88·65	18·8	764

all, the volume of air above the liquid in the flask and in the connecting tubes; a table of corrections to this volume is then drawn up to allow for small changes in the temperature and atmospheric pressure during the experiment.

The alternative method, suggested by Lunge, for eliminating the air in the reaction flask by replacing it by water introduced through a tap funnel has proved not to be so accurate owing to the reduction in the volume of gas that can be collected in the burette, and the fact that gas bubbles tend to collect in the stem of the tap funnel and cannot easily be dislodged.

The pressure-temperature compensator is set in the first place by taking out the tap, t_2, and adjusting the amount of liquid in the manometer arms so that the two columns are level at atmospheric pressure, a few c.c. of 1 per cent. sulphuric acid being put in the compensator bulb. Readings are taken of the temperature of the water-bath and the atmospheric pressure, and the correction factor for reducing any volume of gas in the burette to S.T.P. is calculated from these figures as usual. The liquid in the manometer arm is then sucked up to the tap, t_2, the small volume of air between the manometer liquid and the burette being measured and added to all readings made against the compensator.

One setting of the compensator will remain accurate for several weeks, but it is advisable to check its accuracy from time to time. The following is an example of a double check on the compensator and on the calculated pressure

temperature corrections for the air in the flask; incidentally, this test also tended to show: (1) that the apparatus was free from leaks, (2) that there was no absorption of gas by the burette liquid or the soda solution in the flask, (3) that 25 minutes was sufficient time to allow for cooling the flask to the normal temperature.

(4) *Calibration Correction.*—In all cases it is necessary to calibrate the measuring burette before use. These instruments are usually calibrated by the makers to work with mercury, and when used with water, which for the present purpose is much more convenient, they give considerable errors in the readings owing to the differences in the position of the meniscus. The burette was carefully cleaned with nitric acid, potassium dichromate, and water, and was then calibrated in the usual way by filling it with water at a known temperature, and running off and weighing 5 c.c. at a time; a repeat calibration was carried out in which 10 c.c. were run off at a time. From these results the necessary calibration correction curve was drawn. From time to time during use the burette should be again cleaned with warm nitric acid and potassium dichromate.

(5) *Vapour Pressure Correction.*—The ordinary water-vapour correction to the pressure reading is eliminated by the compensator and included in the compensator factor, but there is another vapour-pressure correction which does not appear to have been considered by any other workers, although it seems to be worth enquiry. This correction is necessary to compensate for the change in the mean water-vapour pressure of the air in the flask, between the beginning and end of the experiment whenever gas is collected in the burette. If we suppose we have 100 c.c. of gas in the burette over 1 per cent. of sulphuric acid at 20° C. and 40 c.c. of air in the flask and connecting tubes over 40 per cent. sodium hydroxide solution at the same temperature, then the vapour tension in the flask is 8·7 mm. of mercury and in the burette 17·5 mm. On theoretical grounds it seems that it would be extremely difficult, if not impossible, to calculate the mean vapour tension of the whole system, since the phenomenon is dynamic rather than static, being governed by the rate of diffusion, so that equilibrium would not be obtained in a reasonable time. It is, therefore, probably sufficiently accurate for practical purposes to assume that we have a *uniform gradient* in the water vapour tension from 17·5 mm., that of the 1 per cent. sulphuric acid to 8·7 mm., that of the 40 per cent. sodium hydroxide solution at 20° C. With this assumption the mean water-vapour tension of the air in the flask must vary with the volume of gas in the burette when these are connected together. At the outset there will be no gas in the burette, and the water-vapour tension is then the mean of 17·5 and 8·7 = 13·1 mm.; at the end of the experiment the water-vapour tension will clearly be *less* by an amount, increasing with increasing volume of gas collected in the burette, and in proportion to the sum of the volumes of gas in the burette, flask and connecting tubes. This will produce a *reduction* in the amount of gas collected in the burette, and must be allowed for by the appropriate calculated correction. This correction is very small, and in calculating it the normal temperature-pressure variations of the air may be ignored. As the validity of this correction may be disputed, the actual figures used in correcting my results are given in Table III.

These figures in Table III represent the mean of two possible assumptions: (1) that the whole of the vapour is at the higher pressure; (2) that the whole of the

vapour is at the lower pressure. If we assume (2), which appears to be more in accordance with the experimental results, the maximum correction would be about 0·15 c.c. more than that given in Table V; if we assume (1), without having, so far as we know, any particular justification, then the correction would vanish. It is therefore clear that the assumption of a *uniform gradient* in the vapour-pressure cannot, in any case, introduce an appreciable error into our results, since the figure ± 0·15 c.c. is equivalent to a weight of silicon practically outside the limits of accuracy of the laboratory chemical balance.

TABLE III

VAPOUR-PRESSURE GRADIENT CORRECTION

Volume of flask and connections = 40 c.c.
Assumed mean temperature = 20° C.
Mean atmospheric pressure = 760 mm.

Volume of gas in burette c.c.	Correction to add to measured volume c.c.
0	Nil
10	0·05
20–50	0·10
60–100	0·15

The application of these various corrections is shown by the observations for two typical experiments given in Table IV.

TABLE IV

TYPICAL EXPERIMENTAL OBSERVATIONS WITH CORRECTIONS

Experiment number	842	843
Metal	E	Q
Weight taken	5 grms.	5 grms.
Drying temperature	200° C. for ½ hr.	200° C. for ½ hr.
Atmospheric pressure	758 mm.	758 mm.
Flask temperature before	21·4° C.	21·3° C.
" " after	22·2° C.	21·00° C.
" " correction	− 0·10 c.c.	+ 0·05 c.c.
Burette temperature	21·1° C.	19·8° C.
Condenser water	21·0° C.	19·9° C.
Measured volume of gas	48·10 c.c.	42·20 c.c.
Compensator gas volume	3·75 c.c.	3·75 c.c.
Vapour-pressure gradient correction ..	+ 0·10 c.c.	+ 0·10 c.c.
Calibration correction	+ 0·15 c.c.	+ 0·15 c.c.
Nett volume	52·00 c.c.	46·25 c.c.
Compensator factor	0·9202	0·9202
Volume of gas at S.T.P.	47·80 c.c.	42·55 c.c.
Silicon equivalent	0·0299 grm.	0·02665 grm.
Total silicon in metal	0·0375 grm.	0·0430 grm.
Free silicon in acid residue..	79·8%	62·0%

It must not be thought that the method is in reality very complicated, for once the corrections have been worked out they can be applied to the measured volumes and the result calculated in 2 or 3 minutes. Further, the gasometric determination on the siliceous residue can be completed in under one hour—a very much shorter time than by any gravimetric process.

VERIFICATION OF ACCURACY OF METHOD ON PURE ALUMINIUM.—It was decided, in the first place, to standardise the apparatus and method of working on

pure aluminium, since it was already known from Mallet's atomic weight determinations that aluminium was capable of giving results of the highest accuracy and consistency.

The reaction between aluminium and sodium hydroxide is in accordance with the following equation:

$$2Al + 2NaOH + 2H_2O = 2NaAlO_2 + 3H_2$$

$$2 \times 26{\cdot}97 \text{ grm. Al} \equiv 3 \times 2{\cdot}0154 \text{ grm. } H_2$$

$$1 \text{ grm. Al} \equiv 0{\cdot}11208 \text{ grm. of hydrogen.}$$

But 1 litre of hydrogen measured at S.T.P. weighs 0·08988 grm.

Therefore, 1 grm. of aluminium $\equiv$ 1247·0 c.c. of hydrogen at S.T.P.

The above figures are taken from the International Critical Tables, 1929.

The accuracy possible in these experiments was limited chiefly by the possible accuracy of weighing with the available chemical balances. A "Chainomatic" balance was used, and the weights and the graduated chain column were standardised against a set of standard weights calibrated by the National Physical Laboratory; the true weights of these standard weights were accurately known to ± 0·01 mgrm. It was then possible actually to weigh within ± 0·05 mgrm., and the weights given may be taken as correct to 0·1 mgrm.

Pieces of pure aluminium metal of convenient size were cut from the inside of a block and cleaned in nitric acid, water, hydrochloric acid and water, dried on filter paper and on the hot plate for 30 seconds, and then left in the balance case for 15 minutes before weighing. They were weighed directly on the balance pan and then wrapped up in a small dry filter paper and kept in the desiccator ready for use.

The determinations were carried out as previously described, the reaction between the 40 per cent. sodium hydroxide solution and the aluminium being allowed to proceed with gentle warming; finally, the liquid was boiled to complete the reaction. Some determinations were also carried out on a standard sample of aluminium-silicon alloy containing 11·60 per cent. of silicon; these experiments showed a similar degree of accuracy to those on pure aluminium, from which it may be concluded that the method is likely to be as accurate for the determination of silicon as for that of aluminium. The results of these standardisations are given in Table V.

The results of Table V, as a whole, show an accuracy of ± 0·2 per cent., which may be regarded as satisfactory.

GASOMETRIC ANALYSIS OF PURIFIED SILICON.—Having shown in the previous experiments on aluminium of known purity that the measured volume of hydrogen in our apparatus is chemically equivalent to the weight of aluminium taken, we may conclude that our apparatus and method of working are satisfactory. The next stage is evidently to show a similar relation between hydrogen and silicon; the method should then be satisfactory for the determination of silicon.

Several samples of high purity silicon were therefore prepared by the method employed at the National Physical Laboratory.* By this method it is claimed

* N. P. Tucker (*J. Iron Steel Inst.*, 1927, 48).

that it is possible to obtain a material containing 99·94 per cent. of silicon, but, as apparently the author did not investigate the question of silica in this material, there is some doubt as to the accuracy of his figures.

TABLE V

STANDARDISATION OF GASOMETRIC METHOD AGAINST ALUMINIUM

Exp.	Weight taken Grm.	Volume of hydrogen corrected to S.T.P. c.c.	Equivalent weight of metal Grm.	Determined Per Cent.	Iron in Al Per Cent.	Al found as per cent. of Al taken
250	0·07590	94·66	0·07590	100·0	0·11	100·1
251	0·07500	93·41	0·07491	99·88	0·02	99·9
252	0·07435	92·53	0·07420	99·80	0·02	99·8
253	0·07390	91·97	0·07375	99·8	0·06	99·9
203	0·07000	89·45	Aluminium-silicon alloy containing 11·60% Si	99·3	0·40	99·7
204	0·07000	89·85		99·7	0·40	100·1
255	0·07050	90·19		99·3	0·40	99·7
Effect of iron on the standardisation.						
260	0·0135 Fe	0·10 (about)	—	—	—	—
261	0·0114 Fe, 0·007585 Al	94·47	0·07576	99·88	0·06	99·94

Note on Table V.—The metal used for experiments 251, 252 was Hoopes metal (99·9 per cent. Al, 0·06 per cent. Si, 0·02 per cent. Fe, 0·02 per cent. Cu); the metal for experiment 253 was virgin ingot metal of 99·8 per cent. purity (0·09 per cent. Si, 0·06 per cent. Fe, 0·006 per cent. Ca, 0·003 per cent. Mg, 0·003 per cent. Cu), while the metal of experiment 250 was some high-purity wire showing no appreciable amounts of impurities except iron and silicon. The amounts of silicon in the metal of experiments 250 to 253 were found by the ordinary gravimetric process to be between 0·06 and 0·12 per cent., and as silicon evolves hydrogen with caustic soda, it is included with the aluminium, the difference between the equivalent volumes being quite negligible (*e.g.* for 0·06 per cent. of silicon we would get a difference of 0·014 per cent. in the final figure). For the aluminium-silicon alloy experiments Nos. 203, 204, 255, the percentage figures given in the final column of Table V represent the per cent. of aluminium estimated, assuming the theoretical volume of hydrogen equivalent to 11·60 per cent. of silicon (the figure 11·60 per cent. of silicon is the mean of nine standard determinations by the soda method, and is probably correct within ± 0·05 per cent. Si) and subtracting this volume from the total volume of hydrogen at S.T.P. The final experiments of Table V are included to show that the amount of iron in the metal of experiments 250 to 253 can have no effect on the results.

There is, however, some basis for the assumption that the silica in silicon prepared by the N.P.L. method will be reduced to a minimum, for in the method of treatment the material is "fumed" five or six times with hydrofluoric and sulphuric acids, and at the same time independent tests show that a single fuming will usually remove, so far as can be detected by the loss of weight, any silica added to the material. The possibility of appreciable silica in solution in the silicon is practically excluded by the very different shapes of the space-lattice of these two substances, for Hull (*Phys. Rev.*, 1917, 9,564, 10,661) has shown that that of silicon belongs to the cubic system, while McKeehan (*Phys. Rev.*, 1923, **21**, 206, 503) has shown the space-lattice of silica to be rhombohedral.

In the method of preparation developed at the National Physical Laboratory, after the hydrofluoric acid fuming treatment the silicon is treated with hydrochloric acid to remove sulphuric acid and iron; and as it seemed there might possibly be a little oxidation here, the metal used for these experiments (Tables VI and VII) was given a final treatment with hydrofluoric acid only.

The hydrofluoric acid was "fumed" off on the hot plate, and the silicon weighed and then dried for two further periods of half an hour on the hot plate. The changes in weight during this drying with the sample of purified silicon used are given below, together with the effect of ignition of a small sample of the same material. These figures show that the method of drying, while removing all but a minute trace of volatile matter, produces a scarcely appreciable amount of oxidation.

Drying Purified Silicon.

(i) Weight of purified silicon taken .. .. .. = 20·2213 grms.
(ii) Dried half an hour at 200° C. — loss .. .. = 0·0043 grm.
(iii) Dried further half hour at 200° C. — gain .. = 0·0024 grm.

This final dried material (iii) was sealed up in a glass tube and used later for experiments of Tables VI and VII; some of this dried material was ignited, with the following result:

Weight of dried silicon taken .. .. = 0·4965 grm.
Ignited 1 minute over a Bunsen burner — loss = 0·0002 grm.
,, 5 minutes ,, ,, — gain = 0·0006 grm.

It is evident from the above considerations that the purified silicon (the material dried at 200° C., No. 3 above) can contain only very small amounts of silica and non-volatile impurities. The non-volatile impurities were next determined by "fuming" with hydrofluoric, nitric and sulphuric acids, followed by ignition of the residue; four lots of 0·20 grm. each were treated, blanks being run alongside.

Non-volatile impurities (mean) 0·30 per cent.

Five weighed samples of this material (No. 3) were then analysed in the gasometric apparatus, with the results given in Table VI.

TABLE VI

TEST OF GASOMETRIC METHOD ON PURE SILICON

Exp.	Weight of silicon taken Grm.	Volume of hydrogen correct to S.T.P. Per Cent.	Equivalent weight of silicon Grm.	Silicon found Per Cent.
271	0·05785	91·74	0·0574	99·2
272		92·02	0·05758	99·5
273		91·98	0·05755	99·5
274		91·79	0·05744	99·3
275		91·66	0·05736	99·2
			(Mean)	99·3

The results given in Table VI show a similar order of consistency (± 0·2 per cent.) to those obtained for aluminium. Assuming a mean figure of 0·30 per cent. for the non-volatile impurities, these results suggest that the purified silicon may contain 0·4 per cent. of silica.

GASOMETRIC DETERMINATION OF THE OXIDATION OF SILICON.—Since the method gives concordant results for purified silicon, it can be used to trace the progress of oxidation of silicon from the original purified state down to more than 80 per cent. of silica.

In the first series of experiments the oxidation of purified French silicon was measured, and as it was found difficult to trace this beyond 10 per cent., owing to the extremely slow rate of oxidation, a second series of experiments was carried out on finely divided silicon from aluminium-silicon alloy.

For the experiments with purified French silicon about 2 grms. were weighed in a porcelain crucible (F.2) and then ignited for 1 hour, and the increase in weight noted; two samples of 0·060 grm. of this oxidised material (F.3) were then analysed in the gasometric apparatus. The rest of F.3 was again ignited for 4½ hours, and the increase of weight was noted; two samples of this oxidised material (F.4) were then analysed in the gasometric apparatus. The rest of F.4 was again heated for 6½ hours, and the increase of weight was noted; two samples of this oxidised material (F.5) were then analysed gasometrically. The rest of F.5 was heated for a further 7¾ hours, and the increase of weight was noted; two samples of this oxidised material were then analysed gasometrically. The results of these experiments are given in Table VII, together with an explanation of the method of calculation used.

TABLE VII

GASOMETRIC DETERMINATION OF THE OXIDATION OF PURE SILICON

Sample No. before testing	Weight before heating Grm.	Weight after heating Grm.	Ignition increase Grm.	Calculated as SiO_2 ($\times$ 1·877) Grm.	Total SiO_2 Per Cent.	Impurities by HF $+HNO_3$ $+H_2SO_4$ Per Cent.	Silicon (by difference) Per Cent.	Gasometric silicon per cent. (mean) Per Cent.
F.2	1·8864	1·9284	0·0420	0·0789	4·5	0·3	95·2	95·2
F.3	1·8034	1·8177	0·0143	0·0268	5·95	0·3	93·75	93·7
F.4	1·6971	1·7097	0·0126	0·0236	7·35	0·35	92·3	92·1
F.5	1·5869	1·6006	0·0137	0·0257	8·95	0·35	90·7	91·0

The method of calculation employed in this table is as follows:—The composition of F.2 has been taken as 99·3 per cent. of silicon, 0·4 per cent. of silica, and 0·3 per cent. of impurities, as derived from Table VI. For the first oxidation experiment, 1·8864 grm. of F.2 was heated, and the gain in weight, calculated to silica worked out at 0·0789 grm. Hence the total amount of silica in the product (F.3) was 0·4 per cent. of 1·8864 grm. (originally present), *i.e.* 0·0075 grm. plus the 0·0789 grm. gained by oxidation, making 0·0864 grm. of silica in all. The total weight being 1·9284 grm., the final percentage of silica was 4·5 per cent. The impurities, separately determined, were found to be 0·3 per cent., and thus the free silicon, determined by difference, should be 95·2 per cent., a figure identical with that directly determined gasometrically (mean of duplicates). Similarly for the second experiment (oxidation of F.3):

	Per Cent.
Total silicon in oxidised product (F.4) $= \dfrac{(4{\cdot}5\% \text{ of } 1{\cdot}8034) + 0{\cdot}0268}{1{\cdot}8177}$	= 5·95
Impurities	= 0·30
Hence, silicon (by difference)	= 93·75
as compared with a gasometric figure of	93·7

ACCURACY OF GASOMETRIC METHOD.—From the method of preparation of the silicon (F.2), from the consistency of the results in Table VI, and from the close agreement between the two sets of silicon figures in Table VII, it seems clear that there is no appreciable systematic error in the method, and that the assumed composition of the original purified silicon (F.2) is substantially correct; this is confirmed by the further results given in Table VIII.

OXIDATION OF SILICON FROM ALUMINIUM-SILICON ALLOY.—Finely divided silicon was prepared by dissolving 50 grms. of a 15 per cent. aluminium-silicon

alloy in lots of 10 grms. at a time in hydrochloric acid. The residue was washed on a filter and then re-boiled with hydrochloric acid for 30 minutes. It was again filtered off and well washed with hot water. It was then transferred to a platinum basin and "fumed" 5 times with hydrofluoric acid only (if sulphuric acid is here used with the hydrofluoric acid, exceptional difficulty is found in decomposing the aluminium sulphate complexes remaining in the silicon), dried on a hot plate and then in an electric oven at 550 to 600° C. (A.1).

About 2 grms. of this material were then ignited for 5 minutes to remove combined water (A.2) and again strongly ignited for 15 minutes to ensure the decomposition of any impurities present (A.3). Preliminary experiments showed that the above treatment was essential to ensure the complete removal of all volatile impurities in the silicon. The progress of the oxidation was roughly traced by withdrawing samples at the stage A.1, A.2, A.3 for gasometric analysis.

The product was now ready for the quantitative experiments. About 1·5 grm. of A.3 was exactly weighed in an ignited porcelain crucible, and a series of experiments carried out exactly as for the pure crystalline silicon. For these experiments all weighings of silicon were checked twice at an interval of 5 minutes after first standing in the balance case for 15 minutes; the powder was well stirred, re-weighed, and then 2 samples were taken for gasometric analysis, the residue being again weighed before the next ignition. The porcelain crucible containing the silicon was accompanied by a blank crucible which was ignited simultaneously and weighed immediately after or before it. (Platinum crucibles cannot be used for heating silicon owing to the formation of the easily fusible sub-silicide.)

The most important figures from these oxidation experiments are given in Table VIII.

TABLE VIII

GASOMETRIC DETERMINATION OF OXIDATION OF SILICON FROM ALUMINIUM-SILICON ALLOY

Sample	Ignition time	Weight before ignition Grm.	Weight after ignition Grm.	Increase (as SiO_2) Grm.	SiO_2 Per Cent.	Impurities (non-volatile) Per Cent.	Silicon calc. from wt. increase Per Cent.	Silicon by gasometric analysis (mean) Per Cent.
A.4	30 mins. } Bunsen	1·4151	1·4248	0·0182	17·34	1·46	81·20	81·0
A.5	1 hour } burner	1·1843	1·2135	0·0547	21·45	1·43	77·12	77·21
A.6	3 hrs. in muffle	1·0631	1·3210	0·4840	53·90	1·15	44·95	44·95
A.7	2 ,, ,,	0·5998	0·6394	0·0743	62·2	1·08	36·72	36·70
A.8	2 ,, ,,	0·4387	0·4523	0·0255	65·9	1·05	33·05	32·76
A.9	4 ,, ,,	0·2363	0·2510	0·0276	73·2	—	—	—
(Cont'd.)	8 ,, ,,	0·2444	0·2694	0·0469	84·0	0·91	15·09	14·98

The gasometric silicon figures are the mean of duplicates except A.8 (1 only) and A.6 (4 determinations). These figures for A.6 were:—44·8, 44·8, 45·1, 45·1 per cent. of silicon, and the mean of these results was used as the basis for calculating the other figures in Table VIII (as the results for F.2 were used for Table VII). The method of calculation has already been explained under Table VII. The figures underlined in the last two columns are, respectively, those calculated from the increase in weight of the silicon overheating, and those obtained from the hydrogen evolved in the gasometric analysis after oxidation of each residue.

CONFIRMATION OF ACCURACY OF GASOMETRIC METHOD.—The results in Table VIII for the oxidation of silicon from aluminium-silicon alloy show the same order of agreement in the percentage silicon figures as those given for purified

French silicon in Table VII. The agreement between these silicon figures (last two columns of Tables VII and VIII) provides the strongest argument for the accuracy of the method, for if there were an appreciable systematic error in the method, in proportion to the amount of such error the gasometric silicon figures in Tables VII and VIII would be, on the whole, either higher or lower than those calculated from the weight increases, and this quite independently of the composition of F.2 or A.6 used for calculating these tables.

From all the results of Tables VI, VII and VIII we may conclude that the accuracy of the method is of the order of ± 0·3 per cent. If we consider errors of this order in connection with a normal sample of commercial metal containing, say, 0·20 per cent. total silicon, of which 0·05 per cent. is in the free state, the error would be less than ± 0·0002 per cent. on the metal, for 100 c.c. of hydrogen collected in the burette. It should be further noted that in these experiments with a weighed quantity of the silicon, the largest error is probably in the weighing out of the material, but in determinations on the pure metal itself this limitation in the accuracy of weighing is not a factor which can affect the figures for the results, for the original weighing is in quantities of 5 or 10 grms. instead of 0·060 grm. (See note.)

Comparison of Gasometric Method with Gravimetric Soda Process.—It is interesting to compare the results obtained by the gasometric method with those obtained by the gravimetric soda process for the determination of total silicon (*cf.* Analyst, 1932, **57**, 500). The result of such a comparison is given in Table IX.

Table IX

Comparison of Gasometric and Gravimetric Processes

		Gravimetric results		Gasometric oxidation results		
Sample from Table VIII expts.	Wt. taken for gravimetric analysis Grm.	SiO_2 by HF fuming (including SiO_2 from the filtrates Grm.	Total silicon found = SiO_2 × 0·4672 Per Cent. of wt. taken	*A*. Mean silicon of Table VIII last 2 columns Per Cent.	*B*. SiO_2 from Table VIII mean figure Per Cent.	Total silicon in material = A + (B × 0·4672) Per Cent.
A.6	0·05	0·0755 0·0744	<u>70·04</u>	44·95	53·90	<u>70·15</u>
A.4	0·05	0·0955 0·0960	<u>89·47</u>	81·1	17·44	<u>89·25</u>

Note.—Tests showed that the sensitivity of the balance used was only reduced by 10 per cent. for a change of weight on the pans from 0·06 to 10 grms.; the actual reduction in the weighing error in such a case would therefore be about 140 times.

The significant figures in the comparison of the two methods are underlined in Table IX, from which it can be seen that the difference between the mean of the gasometric-oxidation results and the mean of the 4 gravimetric determinations amounts to only 0·10 per cent. When taken in conjunction with previous results with both methods this serves as a mutual and, at the same time, an independent confirmation of their accuracy.

To sum up, the gasometric method has now been tested:—(*a*) on aluminium of known purity; (*b*) on purified silicon; (*c*) against oxygen in oxidation of purified

silicon; (*d*) against oxidation of silicon from aluminium-silicon alloy; (*e*) against the standard gravimetric method for silicon. As the results of these experiments seemed to indicate that the process had a sound basis of accuracy, it was next decided to compare the results which it gave with those obtained by empirical gravimetric methods similar to those referred to at the beginning of this paper.

COMPARISON OF GASOMETRIC ANALYSIS OF SILICEOUS RESIDUES FROM ALUMINIUM WITH GRAVIMETRIC METHODS.—It is possible to make a perfect equable comparison between the two types of methods, for after weighing the siliceous residue from the gravimetric analysis, this same residue is put straight into the flask of the gasometric apparatus and the silicon immediately determined. The results of such a comparison are given in Table X. The gravimetric results were calculated as follows:

If A represents the weight of pure SiO_2 from total silicon determination, and B that of siliceous residue, less non-volatile impurities as determined by methods as given below, the silicon in siliceous residue $= \frac{28{\cdot}06}{32} \times (A—B)$.

TABLE X

COMPARISON OF GASOMETRIC AND GRAVIMETRIC METHODS FOR DETERMINATION OF SILICON IN SILICEOUS RESIDUES FROM ALUMINIUM

	Sample marking		E.	M.	Q.
	Iron (per cent.)		0·29	0·77	0·61
	Total silicon (per cent.)		0·75	0·29	0·86
	Procedure	Method	Graphitic Si (per cent. of total)		
(i)	Metal dissolved in sulphonitric (Method IV, Pt. I) the siliceous residue filtered on asbestos,	Gravimetric	65·6	Nil	60·0
	dried at 200° C., until residue ceases to lose weight.	Gasometric	82·3	42·0	65·0
(ii)	As above, but dried at 550° C. until residue ceases to lose weight.	Gravimetric	59·5	8·5	76·2
		Gasometric	78·6	33·6	60·9
(iii)	As in (i), but dried at 650–700° C.	Gravimetric	36·2	—	—
		Gasometric	71·4	—	—
(iv)	Metal dissolved in mixed acid (Method I, Pt. I) siliceous residue filtered on platinum Gooch	Gravimetric	60·9	50·6	65·6
	crucible and dried at 200° C.	Gasometric	79·6	38·2	61·2

It will be noticed from the results in Table X that the gasometric figures decrease with higher drying temperature; the gravimetric processes, on the other hand, under conditions presumably giving increased oxidation give exactly reversed and anomalous results (M and Q), which make it difficult to give any rational interpretations of the meaning of results obtained by these gravimetric methods. From this lack of concordance between the gravimetric and gasometric results for the same residues from the same metal, we must conclude that these gravimetric figures do not represent, with even a rough approximation, the amount of silicon in these residues. As these results are merely typical of numerous others obtained by gravimetric processes [using procedures similar to those used by Prettner and by Koster and Muller (*cf.* p. 580)], we are forced to conclude that such gravimetric methods are unsuitable for estimating the precipitation of silicon in aluminium.

The results given in this paper with the volumetric process show an accuracy of the order of ± 0·3 per cent., from which it appears that this is by far the best

process at present available for the determination of graphitic silicon in a siliceous residue. The next stage of our investigation, namely, the correlation of the silicon in the siliceous residue with the precipitation of silicon in the metal itself, is essentially a metallurgical question, and I have dealt with it elsewhere ("Graphitic Silicon, Heat Treatment, and the Electrical Conductivity of Aluminium," *J. Inst. Metals*, 1933, **51**, 199).

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The Micro-Analytical Determination of Methoxyl Groups in Liquid Compounds

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Introduction.—The apparatus originally devised by Pregl (*Quantitative Organic Micro-Analysis*, 2nd edition, p. 150) for the micro-analytical determination of methoxyl groups gives satisfactory results for most substances.

Slight modifications in the form of the apparatus have been suggested recently by Rigakos (*J. Amer. Chem. Soc.*, 1931, **53**, 3903). Working with certain polymethoxyl bodies, Ware (*Mikrochem.*, 1930, **8**, 352) finds that it is necessary to use hydriodic acid solution of sp. gr. 1·96 in place of the acid of sp. gr. 1·7 commonly employed. This investigator adopts certain suggestions put forward by Friedrich (*Z. phys. Chem.*, 1927, **163**, 141). One of these recommendations is that the weight of silver iodide obtained should be corrected to compensate for loss due to incomplete reaction of the methyl iodide with the alcoholic silver nitrate solution. The loss is stated to be proportional to the volume of silver nitrate solution used. A constant correction of 0·06 mgrm. for each ml. of silver nitrate solution is suggested.

Most of the substances reported upon by Pregl and others are solids, and very little information is given in the literature concerning the behaviour of liquid compounds.

Experimental.—For the analysis of liquid methoxyl compounds it has been found necessary to modify the apparatus and technique described by Pregl. An account of the experiments which have been made in this connection is given below, together with a description of the apparatus and technique finally adopted.

The reagents (hydriodic acid solution, acetic anhydride, red phosphorus, alcoholic silver nitrate solution) were prepared in accordance with the directions given by Pregl, and, with the exception of the hydriodic acid solution, sufficient of each was made up to satisfy the requirements of the whole of the experiments. The liquid chosen for the analyses was anisole. This was purified by fractional distillation, and its purity was determined by a combustion analysis which gave the

following values:—C, 78·0; H_2, 7·6 per cent. (Theory: C, 77·77; H_2, 7·41 per cent.). The numerous experiments are described briefly under the following main headings:

(1) Experiments with hydriodic acid solution of sp.gr. 1·7
(2) " " " " 1·95 (approx.)

EXPERIMENTS WITH HYDRIODIC ACID SOLUTION OF SP. GR. 1·7.—(*a*) *Apparatus and Technique devised by Pregl.*—The apparatus and reagents were tested by a determination of the methoxyl content of a sample of pure vanillin. The value obtained for OCH_3 was 20·13 per cent. (Theory = 20·39 per cent.). The results obtained with the anisole are given in the following table (Table I). They differ widely from the value required by theory (28·70 per cent. of OCH_3) and exhibit considerable variations among themselves. For these and all later determinations, sintered glass filters were employed for collecting and weighing the silver iodide.

TABLE I

No.		OCH_3 Per Cent.	No.		OCH_3 Per Cent.	No.		OCH_3 Per Cent.
1	..	22·51	4	..	7·57	7	..	16·14
2	..	7·81	5	..	6·29	8	..	16·84
3	..	13·38	6	..	20·99	9	..	16·92

(*b*) *Apparatus modified from that devised by Pregl.*—The modifications were: (1) the provision of a ground-glass joint between the reaction vessel and the rest of the apparatus, (2) the introduction of a second inlet tube at a point immediately above the trap in order that a separate stream of carbon dioxide may be passed through the silver nitrate solution by way of the trap, (3) replacement of the usual side tube of the reaction vessel by a tube sealed through the wall of the vessel and bearing a glass tap to regulate the rate of admission of carbon dioxide into this part of the apparatus.

Several determinations were made in which the anisole was heated with the reagents at the b.pt. for different times prior to sweeping out the methyl iodide by a current of carbon dioxide. Any tendency for the silver nitrate solution to be sucked back into the apparatus was checked by the stream of carbon dioxide passing through the additional inlet tube mentioned above.

Some of the values obtained are given in Table II. They show a slight improvement on the figures given in Table I, but are still very low and inconstant.

TABLE II

No.		OCH_3 Per Cent.	No.		OCH_3 Per Cent.	No.		OCH_3 Per Cent.
1	..	21·41	4	..	17·99	7	..	19·75
2	..	26·88	5	..	14·53	8	..	14·08
3	..	23·57	6	..	16·13	9	..	17·82

No improvement was effected by making the determinations in the presence of larger amounts of catalyst or by varying the kind of catalyst employed. The following catalysts were used in addition to acetic anhydride:—(1) Phenol, alone and mixed with acetic anhydride; (2) carbon tetrachloride; (3) phthalic anhydride.

The efficiency of the last two substances was found to be equal to that of acetic anhydride or phenol. In the absence of any catalyst the reaction proceeded to only a very slight degree.

(*c*) *Modified Apparatus.*—This apparatus differed from the one just described in that the narrow tube situated immediately above the reaction vessel was replaced by a wider tube filled with glass beads. The beads were wetted with a solution of hydriodic acid of sp.gr. 1·7. It was thought that any anisole which might escape from the reaction vessel would be condensed on the glass beads and returned to the hot solution. The values obtained were very low and were not constant. The figures given in Table III are taken from the results of a number of analyses.

TABLE III

No.	1	2	3
OCH_3, per cent.	13·98	19·81	14·59

(*d*) *Apparatus in which the sample can be heated with the reagents under pressure.*—Several types of apparatus were devised for this purpose. The sample was heated under pressure for different lengths of time at various temperatures, and the methyl iodide was finally swept out of the reaction vessel into the silver nitrate solution by means of a stream of carbon dioxide.

It will be seen from the results given in Table IV that a definite improvement has been effected, but that all the values are low and exhibit considerable variation among themselves. No further experiments were carried out with hydriodic acid solution of sp.gr. 1·7.

TABLE IV

No.		OCH_3 Per Cent.	No.		OCH_3 Per Cent.	No.		OCH_3 Per Cent.
1	..	26·44	4	..	20·49	7	..	27·38
2	..	25·98	5	..	22·55	8	..	24·47
3	..	25·37	6	..	23·62	9	..	26·32

EXPERIMENTS WITH HYDRIODIC ACID SOLUTION OF SP. GR. 1·95 (APPROX.).—(*a*) *With the Ordinary Pregl Apparatus.*—On account of the presence of sulphur in the hydriodic acid solution, the trap was filled with a suspension of red phosphorus in 5 per cent. cadmium sulphate solution in place of the usual aqueous suspension.

The anisole, mixed with the necessary reagents, was heated first in a water-bath at 100° C. and finally over a micro-flame. It was observed that variable but definite amounts of hydrogen iodide vapour escaped from the trap into the silver nitrate solution unless very great care was exercised in heating the liquid and in regulating the rate of admission of the carbon dioxide. This difficulty was partly overcome by introducing a second trap in series with the first. The results obtained in a series of determinations are given in Table V. The values compare favourably with those obtained in the experiments with hydriodic acid solution of sp.gr. 1·7 under pressure.

(*b*) *Apparatus consisting of two Reaction Vessels.*—These were connected together through a small condenser and joined to the usual arrangement of traps and delivery tube.

TABLE V

No.		OCH_3 Per Cent.	No.		OCH_3 Per Cent.	No.		OCH_3 Per Cent.
1	..	26·75	4	..	25·19	7	..	26·31
2	..	29·67	5	..	24·92	8	..	25·68
3	..	25·78	6	..	27·69			

The first of these two flasks contained the mixture of hydriodic acid solution (sp.gr. 1·95), acetic anhydride and anisole. About three-quarters of this mixture were slowly distilled into the second vessel, which contained about 2 ml. of hydriodic acid solution of sp.gr. 1·7 heated to the boiling point. A slow stream of carbon dioxide was passed through the apparatus in the usual manner. Three analyses were made and the following values were obtained:

TABLE VI

No.	1	2	3
OCH_3, per cent.	25·59	27·35	24·62

(c) *New Form of Apparatus.*—In this series of experiments satisfactory results were finally obtained. The form of apparatus employed is indicated in Fig. 1, and it is used for the determination of the methoxyl content of a liquid compound in the following manner:

The glass beads enclosed in the tube A are wetted with 1·5 ml. of hydriodic acid solution of sp.gr. 1·7, and the excess is allowed to drain into the flask E and finally poured away through the side-tube B. The two traps, C and D, are half filled with a 5 per cent. solution of cadmium sulphate containing a little red phosphorus in suspension.

The reaction vessel E is now charged with 8 small drops (0·2 ml. approx.) of acetic anhydride, 3 small crystals (40 mgrms. approx.) of phenol, 1·5 ml. of hydriodic acid solution of sp.gr. 1·95, and two small pieces of porous plate.

The test-tube containing the alcoholic silver nitrate solution is put into position (not shown in the diagram), the constrictions at the upper end of the tube P are closed by a drop of distilled water, and the rubber cap L is slipped over the end of the tube as shown in Fig. 1.

The liquid to be analysed is weighed out in the small glass stoppered tube M (Fig. 2) into which it is introduced from a glass tube drawn out at one end to a fine capillary.

The tube M and the stopper are dropped separately into the flask E through the side tube B. The tube F and the adaptor G are now put into position as quickly as possible. A current of carbon dioxide is passed through the apparatus at such a speed that not more than two bubbles of gas appear in the silver nitrate solution every second. The flask is heated in a bath of glycerin, the temperature of which is gradually raised to 125° C. and thereafter maintained at 125° C. to 135° C. for about 45 minutes. The heating bath is then removed, and the precipitate of silver iodide is treated as described by Pregl, and finally weighed with the usual precautions.

When the analysis is conducted in the manner described above there is no risk of hydrogen iodide vapour escaping from the traps into the alcoholic silver

nitrate solution. This has been verified by numerous blank experiments. It has been observed that the hydriodic acid solution (sp.gr. 1·95) of commerce may contain an impurity which gives rise to a precipitate of silver iodide in the alcoholic

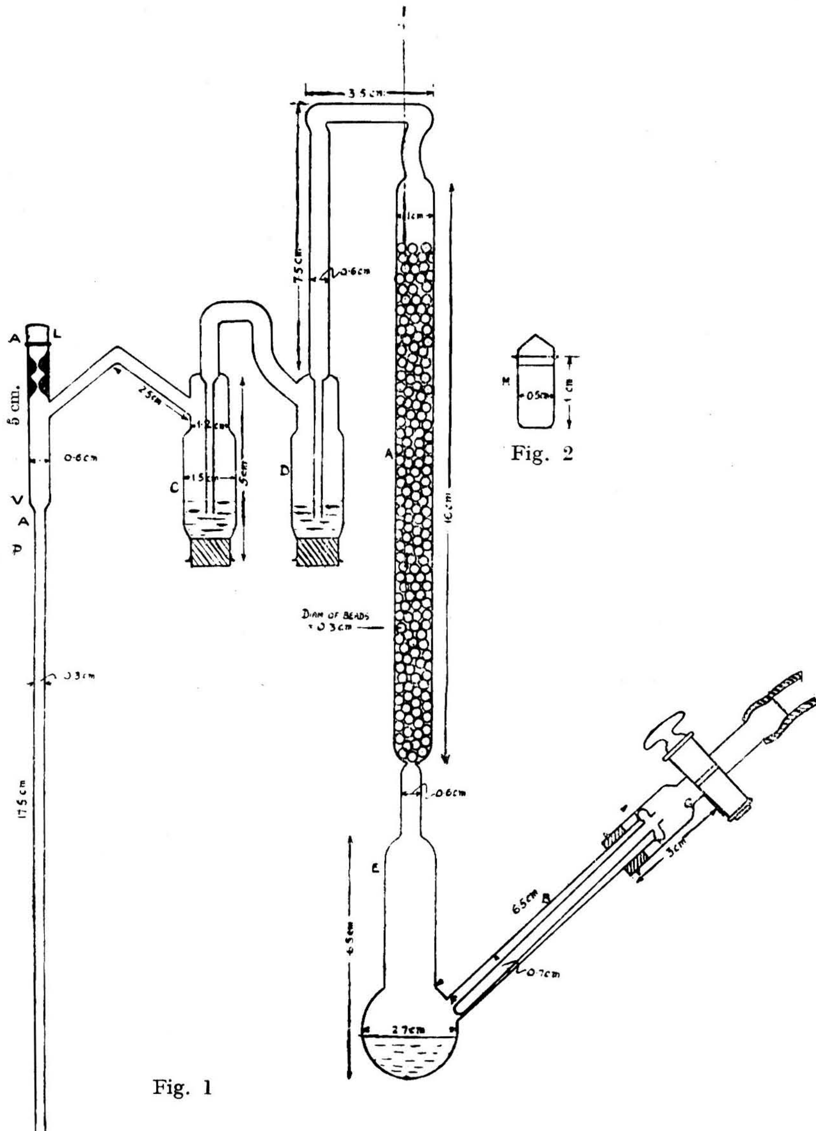


Fig. 2

Fig. 1

silver nitrate solution during an analysis. In one case 9·4 mgrms. of silver iodide were obtained in a blank test in which 1·0 ml. of the hydriodic acid solution diluted with its own volume of water was used. It is therefore advisable to test all fresh supplies of this acid by carrying out a blank experiment before any actual analyses are commenced.

Some results obtained for the methoxyl-content of anisole by the method described above are given in Table VII. Reference has already been made to a suggested correction for loss due to the incomplete reaction of methyl iodide with the alcoholic silver nitrate solution. This correction has not been applied to the figures given in Table VII, because experiments with alcoholic solutions of silver nitrate contained in two tubes connected in series indicated that the absorption of methyl iodide is complete in the first tube.

TABLE VII

No.	Weight of anisole Mgrms.	Weight of AgI Mgrms.	OCH_3 Per Cent.
1	5·662	12·276	28·64
2	5·000	10·839	28·63
3	4·992	10·912	28·87
4	4·977	10·912	28·96
5	4·848	10·460	28·51
6	4·088	8·848	28·60

In conclusion, reference may be made to an improvement in the macro apparatus for the determination of methoxyl groups which has been described by Campbell (*J. Soc. Chem. Ind.*, 1932, **51**, 590). The modification introduced by him consists in heating the liquid in the trap to a temperature of about 55° C. during the analysis. The quantitative removal of the methyl iodide contained in the trap is presumably facilitated by this procedure. An attempt was made to apply this modification to the micro-apparatus described in this article, but the results obtained for anisole were always about 2 per cent. lower than the theoretical value. That the low values obtained may be due to the hydrolysis of the methyl iodide by the warm solution in the traps is suggested by the results of the following preliminary experiments:

(i) A solution of 0·5 ml. of methyl iodide in 100 ml. of water was heated to 60° C. At the end of 10 minutes 10 ml. of the solution were withdrawn, cooled rapidly and freed from dissolved methyl iodide by the passage of a rapid current of air. The iodine-content of the solution was determined as silver iodide. Similar samples were taken at the end of 20, 40 and 60 minutes, respectively, and the iodine content was determined. The following results were obtained:

Time, minutes	10	20	40	60
Silver iodide, mgrms. ..	0·568	0·974	2·084	2·937

(ii) A similar solution was allowed to stand at room temperature (20° C.). The total iodine was determined in 10 ml. of the solution after 0·0 mins. and 60 mins., and the values obtained were as follows:

Time, minutes	0·0	60
Weight of silver iodide ..	Small trace	0·157 mgrm.

In a paper by Bruckner (*Mikrochem.*, 1932, **12**, 153), which appeared after the completion of the experiments described above, emphasis is laid upon the importance of dissolving the methoxy compound in the catalyst reagent prior

to the addition of the hydriodic acid solution. Analytical results are given for a number of compounds, including liquid substances of high b.pt.

The procedure adopted by Bruckner is, briefly, as follows:

(i) The sample is weighed into a small glass cup provided with a glass cap.

(ii) The weighed substance is moistened with a little of the catalyst reagent (*e.g.* acetic anhydride) and is then introduced into the reaction vessel of the ordinary Pregl apparatus containing about 0·1 ml. of catalyst and 0·1 mgrm. to 0·2 mgrm. of phenol.

(iii) When the compound has completely dissolved (with gentle warming, if necessary) the usual volume of hydriodic acid solution of sp.gr. 1·7 is added, followed by about 10 mgrms. of tinfoil rolled up to form a small pellet.

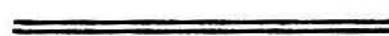
(iv) The remaining stages in the determination follow the directions given by Pregl (*loc. cit.*).

In the table below are given the values which I obtained for the methoxyl content of anisole, employing the technique outlined above. The results indicate clearly that the method is unsatisfactory for the compound in question.

No.	Weight of anisole Mgrms.	Weight of silver iodide Mgrms.	OCH_3 Per Cent.
1	5·503	5·215	12·52
2	4·786	6·930	19·14
3	4·342	4·810	14·63
4	5·922	8·203	18·31

SUMMARY.—Experiments are described which demonstrate that the apparatus and technique originally devised by Pregl give unsatisfactory results for the methoxyl content of those liquid compounds which tend to distil unchanged from the reaction vessel. A number of results obtained for one such compound (anisole) is given, and an apparatus is described which yields correct values for this substance under the proper conditions.

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



Notes

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

THE DETERMINATION OF IODINE VALUES BY THE PYRIDINE SULPHATE BROMIDE METHOD

THE abstract (ANALYST, 1924, **49**, 105) of Rosenmund and Kuhnhenn's paper (*Z. Unters. Nahr. Genussm.*, 1923, **46**, 154) states that tables in the original paper (the journal is not available here) show that the results are "strictly comparable" with those given by standard methods.

With a view to the adoption of this process for routine work a few comparative figures were determined.

(i) *Sesame oil containing about 4 per cent. of mineral oil (probably due to storage in a tin which had contained motor oil).*

Wijs method	104·5	
	104·4	
Margosches alcoholic iodine method ..	102·3	
Hübl method	101·6	
Pyridine sulphate bromide method ..	98·5	(5 minutes' contact, 23 per cent. excess iodine)
	97·9	(5 minutes' contact, 21 per cent. excess iodine)
	98·0	(5 minutes' contact, 46 per cent. excess iodine)
	98·5	(30 minutes' contact, 20 per cent. excess iodine)

(ii) *Sesame oil adulterated with arachis oil.*

Wijs method	105·3
	105·6
Margosches alcoholic iodine method ..	104·8
Hübl method	103·5
Pyridine sulphate bromide method ..	99·7

(iii) *Mixed solid fatty acids obtained from ghee by the method of Cocks, Christian and Harding* (ANALYST, 1931, **56**, 376).

Wijs method	9·89
Pyridine sulphate bromide method ..	9·93

The following results were obtained with samples of various oils:

Oil	Wijs method	Pyridine sulphate bromide method
Sesame	108·2	102·5
	108·3	102·6
Arachis	88·8	84·7
Olive	84·4	82·2
Linseed	181·1	168·7
Safflower	139·5	128·1

The results show that the figures obtained by the pyridine sulphate bromide method can be duplicated and are independent of moderate variations in time of contact or excess of reagent, but that they must be accepted with considerable caution when used for comparison with figures obtained by other methods.

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BEAM'S COLOUR TEST FOR HASHISH

Trolle has recently published a pamphlet,* in which he states that Beam's colour test for hashish is not specific, because: (*a*) one specimen of Indian hemp examined did not give the reaction; (*b*) the reaction was given by plant products other than hashish. The pamphlet includes a long statement by G. Rende (who was engaged on the same case) also asserting that Beam's test is not specific, and for the same reasons as given by Trolle.

Beam did not claim that the test was specific; thus he states (*Wellcome Tropical Research Lab. Chemical Section, Bull.* No. 3, 1915) that "the ordinary extract of *Cannabis indica* of the pharmacopoeia," certain "undoubtedly genuine samples of *Cannabis indica*," and a few plants from the southern Sudan and Uganda "did not respond to the test, or, at most, feebly." He also refers (*loc. cit.*) to his second test (*i.e.* with alcoholic hydrochloric acid) as "a useful presumptive test," and says that a test for the varieties which do not respond to the first test described (*i.e.* that with alcoholic potash) "is highly desirable. This remains to be found."

Lucas (*Forensic Chemistry*, 2nd Ed., p. 294) states that "it has been found, however, that genuine preparations of *Cannabis indica*, such as *Ext. Cannabis Ind.*, B.P., and Merck's purified extract, . . . failed to respond to the test" (*i.e.* that with alcoholic potash) and that "occasionally a hashish plant is found that does not respond to either test."

Beam (*loc. cit.*) also states that "certain oils, *e.g.* origanum and santal, give a similar reaction. . . ."

The criticism (p. 21 of the pamphlet) of the statement by Lucas, that the active principle of Indian hemp has not yet been isolated, suggests that Trolle is not familiar with the recent literature on the subject (*e.g.* that of Cahn in the *J. Chem. Soc.*, 1930, 1931, 1932). Of the two authorities cited by Trolle, Fränkel wrote in 1903 and Caspari in 1926.

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AN ALCOHOLIC STANDARD FOR CIDER

As the possibility of introducing a legal standard (both maximum and minimum) for alcohol in cider has been mooted, it seems advisable to discuss the matter from a chemical point of view in the appropriate journal.

According to Professor B. T. P. Barker, the sp.gr. of apple juice varies from 1·040 to 1·090, and the sugar-content from 7·5 to 20 per cent. Lechartier's table gives the potential alcohol of the corresponding ciders as 5 to 11·5 per cent. (by vol.). These alcohol figures would only be attained if the ciders were fermented to dryness.

The rate and degree of fermentation depend mainly on the nitrogen-content of the apple juice. The minimum of nitrogen in the juice to ensure complete fermentation to dryness, according to Grove (1919), is about 0·01 per cent.

The principal factors determining the alcohol in ciders are the sugar and nitrogen-content of the juices. If sugar is supplied in excess, so as to produce a sweet cider, then nitrogen is the main limiting factor.

In the following series of apple juices the nitrogen was determined and the specific gravities were then made up to approximately 1·082 with dry sugar. Nothing else was added. The juices were then fermented (natural fermentation)

* *Contribution à l'Analyse des Substances Toxiques des Stupéfiants*, by Henri Trolle, Cairo, 1932.

for 21 days at laboratory temperature. Some diluted juices (original gravity about 1·032) are included, the ash of these being 0·13 per cent. (approx.).

	Nitrogen in juice Per Cent.	Alcohol Per Cent. (by vol.)	Extract Per Cent.
A	0·0343	11·05	3·20
B	0·0249	10·38	2·95
C	0·0206	9·90	4·66
D	0·0175	9·63	6·25
E	0·0147	8·09	7·75
F	0·0119	6·63	10·85
G	0·0105	4·73	14·58
	0·0112	4·35	1·03
	0·0075	4·10	1·06
	0·0044	2·98	2·98
	0·0024	2·05	5·08

The sample G represents Devonshire cider apple juice. Cider apples yield juice containing, on the average, 0·01 per cent. of nitrogen (Warcollier, *Cidrerie,* 1928, 34), but the amount varies considerably. When the nitrogen is below 0·006 per cent. the juice ferments very slowly and is prone to cider sickness. One of Grove's samples (*Long Ashton Annual Rept.,* 1919) showed only 0·0033 per cent. of nitrogen. The samples A to F represent the juices of table and culinary apples from the Eastern Counties. Ordinary apple juice, which is being more and more used for cider making, contains, on the average, about 0·018 per cent. of nitrogen, the amount varying from season to season. It is higher in the juice of early and immature (or overripe) apples than in that of properly matured fruit. The nitrogen in the juice largely settles the alcohol-content of the cider. Popular taste demands a sweet cider, and sugar must therefore be in excess. Consequently, for true stability in bottle, the nitrogen must be almost entirely eliminated. One or more crops of yeast must be removed (dried yeast contains about 8 per cent. of nitrogen) until the cider is practically free from nitrogen (0·001 per cent. or less for carbonating). This explains why ciders on the market contain anything from 2 to 10 per cent. (by vol.) of alcohol.

A limit of 5 per cent. of alcohol might suit the growers and manufacturers who specialise in English (and foreign) cider apples, but would be awkward for the growers of English apples in Kent, Cambridge and Norfolk.

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DETECTION OF A BANKNOTE FORGERY BY MEANS OF ULTRA-VIOLET LIGHT

Following a recent successful attempt to forge the notes issued by a bank in China, in which a considerable sum of money was involved, a suspected note was submitted to me for comparison with a genuine note of the same issue. The design was exceedingly difficult to copy, being an elaborate engraving, and printed in several colours, yet the forgery was discovered only when a cashier noticed a duplication of serial number.

Examination under the microscope showed that both notes were engravings, and the possibility of a photographic reproduction was thereby eliminated. Attention was therefore directed to small points of difference which might arise in making a hand-copy of an engraving, and several such points were noted. A useful

method of attack in such cases is to photograph a particular letter (*e.g.* a "W") on both notes, and to measure the angles between the strokes after enlargement.

The design was executed so skilfully that this in itself was not considered sufficient evidence of forgery, and the composition of the paper was therefore determined. As it was important that the notes should not be damaged, a few fibres scratched from the edges were disintegrated on a slide and examined after staining with Herzberg's stain. The genuine note consisted of well fibrillated cotton fibres with traces of chemical wood fibres, whilst the suspected note contained cotton and linen with rather less chemical wood, and had been beaten less. Even these differences, however, are such as may correspond with variations between one making of paper and another, and they are therefore not conclusive proof of forgery.

Inspection in filtered ultra-violet light, however, showed plainly that different dyestuffs had been used to print certain portions of the two notes. The blue letters, for example, which appeared identical in shade in ordinary light were black in one case and pale green in the other in ultra-violet light.

As a detail of importance in the use of the mercury-in-quartz lamp for this purpose, it should be pointed out that the characteristic ultra-violet radiation of the lamp is not attained until about one minute after striking the arc, and that the points of difference noted above were invisible during the first 30 seconds. The actual papers also appeared different in colour under the lamp, *viz.* dirty-white in one case and violet in the other. However, such differences may be produced by variations in the degree of washing or cooking of the pulp, and do not necessarily indicate two sources of origin.

Tests were finally made on the watermarks. That of the genuine note was stable to gentle sponging with ether, but this treatment completely removed the watermark from the forgery. Stamps for the production of artificial watermarks for which a colourless penetrating oil is used as a medium are not unknown, and something of the kind seems to have been used here. It is an interesting fact that, whilst neither watermark was visible by reflected ultra-violet light before treatment with ether, after such treatment only the watermark on the forged note stood out with remarkable clarity, like a design printed in black, although of course it had been rendered quite invisible to transmitted daylight. This can only be ascribed either to an ingredient of the stamping-medium which is insoluble in ether, or to an alteration in the physical nature of the paper due to the impress of the stamp.

Some indication of the nature of the printing process used for reproduction was obtained from the fact that, although the notes had exactly the same overall dimensions, the blank margin between the edge of the note and the engraved design was visibly greater in the case of the forged note. It is most unlikely that the highly-skilled forger responsible for this design would fall into an error of mere dimensions, and the explanation may well be that a wet process was used in one case and that the design had been applied to the wet, expanded paper, and had shrunk with it on drying. This is confirmed to some extent by the observation that the discrepancy was considerably greater in one direction than in the other, as might be expected from the well-known fact that the wet-expansion of paper is ten times greater across the line of orientation of the fibres than in the direction of this line.

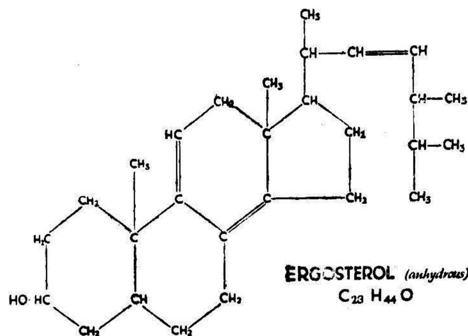
I am indebted to the Directors of Messrs. John Dickinson & Co., Ltd., for permission to publish these results.

JULIUS GRANT

THE LABORATORIES
CROXLEY MILLS, HERTS
July, 1933

STRUCTURAL FORMULA OF ERGOSTEROL

In a paper by Dr. E. L. Smith, Mr. S. G. Stevenson and myself (Analyst, 1933, 129), reference is made to a figure showing the probable structural formula of ergosterol. By an oversight, this was omitted from the text; as a matter of possible interest, I give below the present most generally accepted formula for



the structure of the anhydrous substance, with the reservation then made by us that the position of the double bonds in the ring system is still unsettled.

A. L. Bacharach

THE FORMALDEHYDE TITRATION OF MILK PROTEINS AND ITS USE IN THE DETECTION OF RE-CONSTITUTED CREAMS, ETC.

The formaldehyde titration of milk proteins has been practised for many years, but recently (Pyne, *Biochem. J.*, 1932, **26**, 1006) it has been shown that more reliable titrations can be effected by the addition of potassium oxalate to the sample, thereby eliminating the disturbing effects of soluble calcium salts. The process consists in adding 0·4 c.c. of saturated potassium oxalate solution to 10 c.c. of the milk, then, after the addition of phenolphthalein, adding $N/10$ sodium hydroxide solution until a definite pink shade is developed. Two c.c. of neutral formalin are then added, and the acid so liberated titrated with $N/10$ sodium hydroxide solution until the original colour is produced.

It has been found that a fairly close relation exists between the number of c.c. of sodium hydroxide solution required for the formol titration and the number of c.c. corresponding with the total nitrogen in the same weights of sample.

On applying the process to a number of milks the following figures were obtained; 10 c.c. of the sample were taken for each determination:

	1	2	3	4	5	6	7	8	9	10
Total nitrogen $N/10$ NaOH, c.c.	37·0	33·0	34·5	34·0	35·2	36·5	35·3	36·8	32·2	40·0
Formol titration $N/10$ NaOH, c.c.	2·00	1·85	1·80	1·90	1·85	2·00	1·90	1·90	1·75	2·20
Total nitrogen, c.c. / Formol titration, c.c. ..	18·5	17·8	19·2	17·9	19·0	18·2	18·6	19·4	18·4	18·2

In order to see if the process could be applied to milk powders, 2 grms. of the sample were dissolved in about 30 c.c. of warm water, 0·8 c.c. of the oxalate

solution was added, and the titration was carried out as for raw milk. Total nitrogen was determined on 1 grm. of the powder.

	1	2	3	4	5	6	7	8
Total nitrogen $N/10$NaOH, c.c. (1 grm.)	19·0	26·2	38·0	39·5	32·8	32·0	39·3	36·3
Formol titration $N/10$NaOH, c.c. (2 grms.)	1·5	2·0	2·7	2·8	2·6	2·2	3·0	2·9
$\frac{\text{Total nitrogen, c.c.}}{\text{Formol titration, c.c.}}$	25·3	26·2	28·1	28·2	25·2	29·1	26·2	25·0

According to these figures there is a definite reduction in the number of titratable amino-acid groupings in dried milk protein, as compared with raw milk protein, resulting in a correspondingly higher ratio. It is not intended to examine the reason for this at present, but rather to see if the fact can be applied to the problem of detecting re-constituted creams.

Dried milk powder, particularly the skimmed variety, is cheap and readily worked up with saltless butter into a cream, and, provided the correct ratios are used, such preparations cannot be detected by the ordinary analysis. The Richardson test, depending upon a difference in physical constitution, is in general very satisfactory, but confirmatory tests are always desirable.

From the above tables it will be seen that the highest factor given for raw milk proteins is 19·4, whilst the lowest ratio for dried milk is 25·0—a difference sufficient to distinguish between the one and the other.

When applying the process to cream, between 2 and 3 grms. of the sample are taken for a Kjeldahl determination of nitrogen. Ten or 20 grms. of the sample are placed in a beaker with a little water, and 0·4 c.c. of saturated potassium oxalate solution and phenolphthalein indicator added. The mixture is neutralised with $N/10$ sodium hydroxide solution, 2 c.c. of neutral formalin are added, and the acidity is titrated. The number of c.c. of sodium hydroxide solution required for the total nitrogen per grm. of sample, divided by the number of c.c. required in the formol titration per grm., gives the ratio. This ratio is usually between 17·0 and 19·0 for raw milk, and between 25·0 and 29·0 for dried milk. The following examples may be cited:

Sample	Natural cream	Re-constituted	Re-constituted
Weight of sample, grms.	2·52	2·42	2·55
Total nitrogen, c.c. $N/10$NaOH	4·60	4·0	7·50
Formol titration, 20 grms. = c.c. $N/10$ NaOH	1·90	1·30	2·10
Ratio	19·2	25·5	28·0

It will be noticed that the ratio for the natural cream is within the limits for raw milk proteins, whilst the re-constituted creams were evidently prepared from dried milk. However, further examples are necessary before the value of the test can be established.

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(From the beginning of the Year 1921 to date.)

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CAILLE and VIEL. Detection of Small Quantities of Antimony and Bismuth in Biological Liquids. *Compt. rend.*, 1923, **176**, 1759; *J.C.S., Abs.*, 1923, ii, 585. (Detected by means of antipyrine and potassium iodide.)

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OKAJIMA. Spectral Analysis of Metals, especially Heavy Metals, in the Organs of the Japanese. *Acta Schol. Med. Univ. Imp. Kioto*, 1931, **13**, 417; *C.A.*, 1931, 5463. (Bismuth found in most organs.)

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VALIASCHKO and VIRUP. Determination of Small Quantities of Bismuth in Organic Materials without Decomposing them. *Ukrain. Chem. J.*, 1930, **5** (Sci.), 275; *B.C.A.*, 1931, 702A. (Deposition of the bismuth on a copper plate, precipitation as oxychloride, and colorimetric determination with potassium iodide.)

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Notes from the Reports of Public Analysts

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

CITY OF BIRMINGHAM

Annual Report of the City Analyst for the Year 1932

The total number of samples analysed during the year was 6036, of which 5029 were submitted under the Sale of Food and Drugs Act, representing a purchase of 500 samples per 100,000 of population. Of the samples of food and drugs, 221 were returned as incorrect. There were 2638 samples of milk, of which 171 were adulterated.

Freezing Point of Milk.—The original Hortvet method is the only one used in the laboratory. In order to give the vendor of a milk the benefit of any possible doubt, the figure — 0·530° C. is always used as the basis for the calculation of the percentage of added water.

Cream and Sterilised Cream.—Thirty samples of fresh cream in cuplets or jars and 14 of tinned sterilised cream were examined. The fat-content of the fresh cream varied from 30·5 per cent. to 64 per cent., with an average of 52 per cent. The sample containing 30·5 per cent. had the words "Thick Rich Cream" printed on the carton. Since rich cream, as shown by the average above, should contain at least 50 per cent. of fat, this was a false label, and the vendor was cautioned. Apart from this sample, the lowest fat-content of the fresh cream samples was 43·5 per cent.

The amount of fat in the samples of tinned cream varied from 19·5 per cent. to 28 per cent., with an average of 23·5 per cent.

It will be noticed that, as usual, the amount of fat in the sterilised tinned cream was, on the average, less than half that contained in fresh cream. Unfortunately, while the percentage of fat is usually stated on a tin of sterilised cream, there is no such statement given on a carton of fresh cream, so that the purchaser is unable to compare the quality of the two articles.

One sample contained 24 per cent. of fat, and the label bore the words "A highly concentrated and rich cream." This was a false label, since rich cream should contain at least 50 per cent. of fat, and the packers were cautioned (see also Analyst, 1933, 224).

Labelling of Mineral Waters.—A sample, made in the usual way from essences, had a label describing it as "Orange and Kola." A picture of oranges and kola nuts also appeared on the label, the implication being that the product was made directly from these two articles. There was no justification whatever for this, and the bottlers were cautioned.

Tea "Without Tannin."—Fourteen samples of tea were examined, and one of these, according to the label, contained no stalk and no crude tannin. The amount of stalk present was about 2 per cent., which was quite reasonably in accordance with the label, but tannin was present to the extent of about 15 per cent. When this fact was pointed out to the packers they agreed to withdraw the reference to tannin.

Since 1929 six different brands of tea, all having references on the labels to the absence of tannin, have been examined, and in each case the packers have, on their attention being called to the fact that the tea contained tannin in about the same amount as any other tea, agreed to omit any reference to tannin on the label (*cf.* Analyst, 1933, 400).

"ACID" VINEGAR.—A sample, described as "acid" vinegar, bore a label stating that it was pure acetic acid of about 60 per cent. strength, and, further, that one table-spoonful would make about half-a-pint of table vinegar on dilution with water. Analysis showed that it was practically pure acetic acid of 34 per cent. strength, and not 60 per cent. as stated. The diluted product, made according to the directions given, would contain only about 1·7 per cent. of acetic acid; and even if the sample had contained 60 per cent. of acetic acid, the strength of the diluted article would have been only 3 per cent. Apart from this, table vinegar should be malt vinegar, and not merely a diluted solution of acetic acid. The vendor stated that the article was intended for sale during the Passover celebrations, malt vinegar not being allowed. They agreed to withdraw the label.

H. H. BAGNALL

(See also Quarterly Reports, ANALYST, 1932, **57**, 519; 1933, **33**, 224.)

GOVERNMENT OF MADRAS

REPORT OF THE PUBLIC ANALYST FOR THE YEAR ENDING SEPTEMBER 30TH, 1932

DURING the year under review 3183 samples were taken under the Prevention of Adulteration Act, and of these, 1123 were adulterated. The principal samples were 469 of tea (56 adulterated), 87 of butter (32 adulterated), and 612 of gingelly oil (158 adulterated). There has been a definite increase in the fines inflicted, following comments made in the last Annual Report (ANALYST, 1933, 35), but in several municipalities the fines are still very much too low to have any real deterrent effect. The percentage of adulteration has fallen, but this figure should not be interpreted as meaning that less adulterated food is sold.

DECLARATION OF ADULTERATION.—During the earlier part of the year food vendors in Madras discovered that they were immune from prosecution if, when they sold a sample, they made a verbal declaration that it was adulterated. This difficulty has been got over in two ways. New rules under the Act were issued in September 1932, and in connection with ghee containing other fat in admixture, it is now obligatory on vendors to label it with a printed label in the prescribed form showing the composition of the mixture. In the absence of such a label, a verbal declaration is now no defence. Further, verbal declarations are usually made only to inspectors, who unavoidably become known in their districts. This has been met in Madras City by the employment, by the inspectors, of agents, who are frequently changed, to purchase their samples. Outside Madras City, however, purchase by agent has not been generally adopted.

MILK IN RESTAURANTS.—A defence sometimes put forward when cases are heard is that coffee hotels and restaurants are entitled to add water to milk which they keep for supply to customers either in coffee or as a separate article. This defence is available only when the vendor can prove that in no circumstances is he prepared to supply milk alone. The Act as amended now says that the Court may presume that "any food found in the possession of a person who is in the habit of storing like articles of food for sale has been stored by such person for sale." Accordingly when milk is found in the possession of a hotel-keeper who is in the habit of selling milk as such, there can be no question but that a prosecution lies. The addition of water to milk prepared for sale is now prohibited in the rules made under the Act, and neither declaration nor labelling is any defence.

PRESCRIBED MEDICINES.—In the case of drugs a tolerance of 10 per cent. error is allowed. Mixtures in which the error in dispensing an essential ingredient exceeds this amount are classed as adulterated. Eight mixtures were certified as inaccurately dispensed.

H. HAWLEY

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.

FORMULA FOR PARRISH'S FOOD

ON September 4th a druggist was summoned at Tower Bridge Court, London, for selling "Parrish's Food" deficient in iron to the extent of 73 per cent. and in tricalcium phosphate to the extent of 40 per cent.

The defendant stated that, prior to 1932, there was great variation in the quantities of the ingredients in Parrish's Food, every manufacturer having his own idea of the correct formula and endeavouring to make the preparation as palatable as possible. The B.P. formula was a very strong mixture, and, in the opinion of many people, was not the best, since it threw down a deposit after a few days. He had known such variations as these from the B.P. formula in standard preparations. The bottle in question was part of stock supplied by a reputable firm of wholesale manufacturing chemists.

Mr. P. H. Smith, B.Sc., said that the formula had been used by the manufacturers for the past fifty years, and agreed approximately with that used by other manufacturers.

Dr. H. F. S. Blucke said that he had known of Parrish's Food for the past fifty years. It had been prepared from various formulae, and that used for the preparation before the Court was one of the recognised formulae. In cross-examination, the witness admitted that if he asked for "Parrish's Food" to-day he would expect to receive a preparation made according to the B.P. formula.

The Magistrate (Mr. Campion) said there was no doubt that the "Food" in question was not made up according to the B.P. formula. It could be sold, provided that there was some indication on the label that it did not profess to be the B.P. preparation. He rather sympathised with the defendant, who had bought the business only three weeks before, and was found selling an article which he had no reason to doubt was in accordance with the B.P. He thought that the wholesale manufacturers were to blame, for they should have called in all their stock as soon as the B.P. formula came into being. He would dismiss the summons under the Probation of Offenders' Act, and order the defendant to pay three guineas costs.

Department of Scientific and Industrial Research

REPORT OF THE FOOD INVESTIGATION BOARD FOR THE YEAR 1932*

THE Report is on the same general lines as that for 1931 (ANALYST, 1932, **57**, 715). The General Report of the Board (pp. 1–14) is followed by the Director's Report of the various sections (pp. 15–180). The work of the Torry Research Station is then dealt with (pp. 181–205), that of the Ditton Laboratory (pp. 205–265), and, lastly, the Extra-Mural work, comprising researches at the National Physical Laboratory under the direction of the Engineering Committee, and at the Imperial College of Science and Technology.

SECTION A. MEAT.—Deterioration of meat and fish on storage is due to the interplay of three factors—the increase of salt concentration caused by formation of ice; this results in change of acidity in the tissue, and decrease of chemical

* Obtainable at Adastral House, Kingsway, W.C.2. Pp. 304. Price 5s. 0d.

change owing to fall of temperature. Rate of deterioration is greatest at −2 to −3° C. and decreases almost to zero at −20 to −25° C. Continued work on the changes in fats during storage shows that, whereas samples of fat stored in air developed taint after 2 to 3 weeks at 0° C., those stored in an atmosphere containing carbon dioxide showed greatly increased resistance, but amounts of carbon dioxide over 20 per cent. produced but little further effect. The inhibiting effect appears greatest when other conditions are also unfavourable for the growth of micro-organisms. Carcases which have received careful handling can ordinarily be stored at 0° C. for periods up to 8 weeks, but in small joints the lean is exposed, and at similar temperature could only be kept up to 7 days; previous degree of infection, however, is a very important factor. At 0° C. and 100 per cent. relative humidity, with a bacterial count of 43 per sq. cm., the period is 18 days, but with a count of 17,000 it is only 10 days.

FRUIT AND VEGETABLES. *Gas Storage Conditions.*—Particulars for successful gas storage of four further varieties of apples (Lane's Prince Albert, Annie Elizabeth, Cox's Orange Pippin and Ellison's Orange) have been worked out.

Gaseous Products of Ripe Apples.—The American observation, that ripe apples in a clamp of potatoes retarded sprouting of the potatoes, has led to a search for the active substance in the apple vapour. Germinating seeds of the common pea are conveniently used to check the presence or absence of this substance, since their growth may be almost completely inhibited if sufficient is present, and with smaller concentrations greatly modified; the rate of respiration of such inhibited seedlings is unchanged, although the effect of "apple air" on other apples is to increase their rate of oxidation. The active constituent of the volatile products from apples is not removed or reduced in concentration below the toxic limit, by caustic soda (20 per cent.), alkaline permanganate (saturated potassium permanganate in 15 per cent. caustic soda), acid permanganate (saturated potassium permanganate in 10 per cent. sulphuric acid), iodine (3 per cent. in potassium iodide), sodium meta-bisulphite (saturated), acid cuprous chloride (saturated), shredded paraffin wax, warm olive oil, ammoniacal silver oxide (10 per cent. silver nitrate in ammonia), or by 1 per cent. palladium chloride. Both olive oil and water, however, will absorb sufficient to produce an inhibiting effect when peas are subsequently germinated over these liquids. Complete combustion over copper oxide removed the active constituent, and the yield of carbon dioxide was equal to a concentration of 1 in 28,000 volumes of air. Bromine, ozone, fuming nitric acid, and fuming sulphuric acid at room temperatures also remove the active substance; it is assumed that the substance is ethylene, and it is present only to the extent of about 1 part in 30,000. Pears appear to give off a similar poisonous substance, but, so far, it has not been found in orange or banana air, although there is some indirect evidence of its presence in the banana air.

Concentration of Orange Juice by evaporation does not give a product equal in flavour to the original juice, but preliminary work on concentration by freezing appears more promising.

Effect of Sugar Concentration on Rate of Respiration.—A range of sugar concentration from 0·2 to 7·0 per cent. can be produced in stored potatoes by varying the temperature, and during a study of the internal conditions it was found that low temperature produced a lasting depression of the activity of the respiratory mechanism, perhaps owing to the slow accumulation of an inhibiting substance.

Tomatoes appear to keep better in gas than in air at all temperatures, but for air 12° C. is the best temperature, and the best conditions of all for their storage were an atmosphere containing 5 per cent. oxygen and 5 per cent. carbon dioxide at this temperature.

Freezing Experiments.—The freezing experiments on strawberries, raspberries, sweet cherries and plums have been extended to gooseberries, black and red currants and Morella cherries.

CANNING.—In continuation of the studies on the corrosion of tinplate it has been shown that, whilst small quantities of tin in solution retard the rate of corrosion of iron by acids, small traces of ferrous salts, and, to a less degree, those of copper, increase the rate of corrosion of tin in the presence of oxygen. The action of ferrous salts on the rate of corrosion of iron itself is similar. The effects of small amounts of soluble salts of various metals used in the construction of commercial plant on the colour of raspberries, strawberries and black currants have been studied, and a table of results is given. Although, when present in small quantities, copper, aluminium, nickel, monel metal, stainless steel, silver, tinned copper, silver-plated copper and chrome nickel alloy cause little or no discoloration of the anthocyanin pigments, the metals of tinplate cause much trouble with richly pigmented fruit, and iron acts on the tannins and allied substances, *e.g.* in strawberries.

FISH.—In the study of smoking of fish in order to assess the relative importance in drying of temperature, relative humidity and rate of movement of the air, preliminary experiments have been undertaken in a wind tunnel. Work on the flora in general of the slime and intestinal contents of fresh haddocks from the North Sea has been continued, and in particular on the luminous bacteria.

Luminous Bacteria of Fish.—For these the optimum concentration of sodium chloride for growth appears to be 0·5 to 1·5 per cent., but the cultures used had been growing for 1 to 3 years on a medium containing 0·5 per cent. of sodium chloride and may have become acclimatised to this concentration. Repeated sub-culturing is being carried on to find if this maximum growth is a constant feature. The optimum temperature was 20° C., and at 30° and 37° C. there was no apparent growth. At a temperature of −6° and −12° C. there was a marked initial drop in the numbers of organisms from the superficial slime of the haddock, and this was followed by a continuous slow fall and there was no evidence of increase in numbers during 8 months. At −2° C., however, the initial drop was followed, after 6 to 8 days, by a rise, which continued until the fish was stale.

During the work on the chemical classification of the oils and fats of fishes, lauric acid has been found in the blubber of the porpoise.

VITAMIN *A* IN HALIBUT LIVER OIL.—The extended investigations into the variations of potency in vitamin *A* of halibut liver oil have placed the limits at 30 and 7600 Carr-Price units, and the values have been spectroscopically confirmed in every case. A trial of the sample with a series of rats showed a striking agreement between the blue and biological values. No correlation could be found between potency and position of fishing ground or contents of stomach; nor any relation between the glycogen in the liver (as an indication of general state of nutrition) and vitamin *A* potency, nor was any steady seasonal variation observable. But all the exceptionally rich batches of liver were found in May (also some poor ones), suggestively about a fortnight later than the large seasonal increase found, in 1932, of the plankton of the Irish Sea, and hence of the maximum supplies of carotene.

The relative amounts of *glycogen and lactic acid found in fish muscle* after 4 days' storage at −10° C. seemed to show an unexpectedly high rate of change at this temperature, but further work has established that most of the change actually occurred during freezing.

D. G. H.

Fuel Research.

METHODS FOR THE QUANTITATIVE ANALYSIS OF COAL ASH*

DR. F. S. SINNATT, Director of Fuel Research, states, in a prefatory note, that the Fuel Research Survey Papers, consist of a series of special papers and reports on matters connected with the physical and chemical survey of the national coal resources.

The analysis of coal ash, which was formerly largely a matter of scientific interest, has recently become of considerable practical importance on account of the possible action, for example, of some of the constituents as catalysts in certain processes of coal treatment. As there is no recognised scheme for the analysis of coal ash, and as the need for uniform methods is becoming increasingly felt, the present paper is put forward in the hope that it will form a basis upon which to build a complete collection of methods for all types of coal ash and all constituents that may occur in them. The paper does not purport to be a treatise on the subject.

The methods described have been selected, after extended trials and with such adaptations as experience has shown to be desirable, from those already recognised for the analysis of silicate rocks and other materials similar in composition to coal ash. Throughout the whole of this work the closest touch has been kept with the Geological Survey and the Government Chemist, to whom acknowledgments are made.

The Paper is divided into an Introduction, eight practical Sections and an Appendix.

The Introduction summarises the constituents of coal ash, and gives the limits for the chief constituents in American and British coal ash, with a table of specimen analyses. Section II describes in detail the method recommended for the determination of silica. III deals with the determination of iron, titanium and aluminium, a "cupferron" method of precipitation being used for titanium; IV with calcium and magnesium; V with manganese; VI with sulphur trioxide; VII with the determination of alkalis; VIII with phosphorus, giving the original method of the Fuel Research Board, and an alternative "citric-oxalic-magnesium" method which is put forward tentatively, awaiting the confirmation of further experience.

The Paper concludes with a list of reagents, a bibliography of the references cited in the text, and an Appendix containing a bibliography of the less common constituents of coal and coal ash, classified alphabetically under 22 headings.

* Physical and Chemical Survey of the National Coal Resources, No. 28. By J. G. King, Ph.D., F.I.C., and H. E. Crossley, M.Sc., A.I.C. Pp. 20. Published by H.M. Stationery Office, Adastral House, Kingsway, London, W.C.2. 1933. Price 6d. net.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs Analysis

Manganese-contents of Cows' Milk, Beef, and certain other Foods. G. Büttner and A. Miermeister. (*Z. Unters. Lebensm.*, 1933, **65**, 644–645.)—For the manganese determinations carried out, use was made of Tillmans and Mildner's method, the manganese being oxidised to permanganate and this determined colorimetrically. Three samples of Berlin mixed milk contained from 0·0144 to 0·0173 mgrm. of Mn_2O_3 per 100 c.c., and two stall samples (Berlin) 0·0173 and 0·0058 mgrm., respectively. Five samples of Westphalian milk from individual cows were examined; three gave 0·008, one 0·029, and one (colostral milk) 0·031 mgrm. These results agree well with those recorded by Richards (ANALYST, 1930, **55**, 554; 1931, **56**, 54). Berlin tap-water contained 0·040 mgrm. and two Westphalian waters 0·144 and 0·245 mgrm., respectively, of Mn_2O_3 per 100 c.c. Two samples of lean beef showed undetectable quantities, and three others 0·007, 0·004, and 0·003 mgrm., respectively, of Mn_2O_3 per 100 grms. Raw raspberry juice contained 14·9 mgrms., raw cherry juice 1·4 mgrm., and cranberries 12·8 mgrms. of Mn_2O_3 per 100 grms.

The results obtained for milk and beef differ widely from those given by R. Berg (*Die Nahrungs- und Genussmittel*, 5th Edition, Dresden, 1929), who states that cows' milk contains 66 mgrms., and lean beef 19·8 mgrms. of Mn_2O_3 per 100 grms. T. H. P.

Truffle Sausage containing *Tubiporus rufus* Schff. M. Brüllau. (*Z. Unters. Lebensm.*, 1933, **65**, 645–646.)—Microscopic examination of truffle sausages, which are now being sold in large quantities at low prices, reveals the presence of hyphal tissues, but not of fruit bodies, whereas, if truffles (*Tuber bromale*), or even truffle residues, were used in the preparation, asci should be readily detectable. Large fragments resembling truffles can be separated, and these show a distinct tubular layer and occasional spores. The results of the examination indicate that the fungus in question is possibly *Tubiporus rufus* Schff., which becomes black when boiled. T. H. P.

Dialysis of Milk. Distribution of Phosphorus. L. H. Lampitt and J. H. Bushill. (*Biochem. J.*, 1933, **27**, 711–722.)—Until some method is devised whereby the constituents of milk can be separated by physical means, or without the use of chemicals which themselves react with the milk, no definite hypothesis concerning the composition of milk can be free from criticism; dialysis and ultrafiltration are the methods of separation least open to criticism. The progress of the dialysis of milk can be followed by tracing the changes in the distribution of any of the numerous dialysable constituents, and in this study phosphorus (inorganic and organic) was the constituent chosen. The results obtained could not be compared with those of other workers as there was lack of conformity, owing to variation in the milk and in the apparatus used. A continuous dialysis

apparatus, using collodion thimbles, which is described and shown in diagram, enables dialysis to be carried out at a low temperature (0° to 5° C.), and by its means the dialysate can be concentrated to a convenient volume and the volume of distilled water used brought to a minimum. By the application of a negative pressure to the outside of the dialysing sac, ultra-filtration is combined with dialysis. Dialysis of milk by this means was compared with that by a "static" dialysis method developed by Wardlaw (*J. Roy. Soc.*, 1914, **48**, 252), in which minimum dilution of the milk occurs; the dialysate so obtained was compared with an ultra-filtrate. In all cases collodion thimbles were used. Comparisons were made between the determined amounts of total and inorganic phosphorus in the dialysis fractions and in the ultra-filtrates. It is shown that the serum obtained by "static" dialysis of a solution of spray-dried separated milk powder has approximately the same total and inorganic phosphorus-contents as has that of an ultra-filtrate from the same solution. A similar comparison of continuous dialysis with static dialysis, using fresh separated milk, shows that the former method causes much more phosphorus to be dialysable, and that this increase is confined entirely to the inorganic phosphorus, the dialysable organic phosphorus being the same in both cases. About 37 to 44 per cent. of the phosphorus is in the dialysable form in separated milk powder "solution," and 46 per cent. in liquid separated milk; 60 per cent., however, becomes dialysable under the conditions of continuous dialysis. The results recorded show a certain constancy in the phosphorus distribution of the particular brand of spray-dried separated milk used. These results, when compared with similar ones obtained with bulked liquid-separated milk, support the contention of other workers that heat treatment reduces the inorganic phosphorus of the serum obtained by dialysis or by ultra-filtration. Sufficient evidence has not yet been obtained to make a definite statement regarding the distribution of phosphorus in milk and spray-process powder made therefrom, but there are indications that the heating, or it may be the desiccation, causes slight alterations in the relative amount of phosphorus dialysable. P. H. P.

Determination of Reducing Sugars by Titration of Ferricyanide. S. W. Cole. (*Biochem. J.*, 1933, **27**, 723–726.)—A rapid and accurate method is described for the determination of reducing sugars by the direct titration of boiling alkaline ferricyanide containing a drop of methylene blue as an internal indicator. The indicator is not reduced until the whole of the ferricyanide has been reduced, and the end-point, being a change from a blue or violet solution to one that is colourless, is unmistakable. For the titration, 20 c.c. of a 1 per cent. potassium ferricyanide solution and 5 c.c. of 2·5 *N* sodium hydroxide solution are placed in a 100-c.c. flask with a pinch of broken porcelain and one small drop of methylene blue (1 per cent. in water). To the cold mixture is added all but about 0·2 c.c. of the volume of sugar solution judged to be necessary from a preliminary trial (roughly 1 c.c. of a 2 per cent. or 2 c.c. of a 1 per cent. solution of glucose are required). The mixture is heated to boiling in about $1\frac{3}{4}$ minutes, and the flame is then lowered a little, so that the liquid boils gently. After 1 minute the remaining sugar solution is added, a drop at a time, from a graduated burette (the condensing steam washes the drop off the end of the pipette), at 10 or 15 second intervals, until the end-point

is reached. The total boiling time should be over 2 minutes, and must not exceed 3 minutes. Equivalents are given for glucose, maltose and lactose. A method for the determination of sucrose is described. Details are given for the determination of lactose in milk and of glucose in urine, and a method is described for the determination of maltose and glucose in a mixture of these sugars. P. H. P.

Action of Various Sugars on the Reaction of Sodium Molybdate Solutions. P. Thomas and Mlle C. Kalman. (*Compt. rend.*, 1933, **197**, 330–332.)—It has been found previously (*ibid.*, 1933, **196**, 1672) that the acidification of borax solutions produced by the addition of different sugars no longer takes place when the initial p_H value of the borax solution is 3. The effects of adding laevulose, xylose, galactose, and mannitol to $M/6$ sodium molybdate solutions of various degrees of acidity (p_H, 3·2 to 9·5) have now been studied. At p_H 5·65, the acidity is unaffected by addition of these substances. As the original acidity of the molybdate solution is increased, the additions increase the acidity still more; thus, mannitol at $M/6$ concentration changes the p_H from 5·5 to 5·1. On the other hand, molybdate solutions of higher p_H value than 5·65 are rendered more alkaline by the additions; an original p_H value of 5·8 becomes 7·2 in presence of mannitol at $M/6$ concentration. These changes of p_H in either direction pass through maxima at a certain p_H value, and when the latter is originally about 8, the effects become zero again. The numerical effects of the different added compounds on the reaction diminish in the order: mannitol, laevulose, xylose, galactose. T. H. P.

Sulphur and Phosphorus in the Various Parts of the Wheat Grain. G. Bertrand and L. Silberstein. (*Compt. rend.*, 1933, **197**, 285–288.)—The sulphur-contents of plants are much higher than formerly thought, and plants require to be supplied with sulphur as sulphates to as large an extent as with phosphorus as phosphates. For determining the sulphur- and phosphorus-contents, methods based on analysis of the ash give low results. Using the accurate methods already described (*ibid.*, 1929, **189**, 886), the authors have examined various products obtained from a mixture of home-grown (French) wheat (82 per cent.), Danubian (6), hard winter (6), and Moroccan (6), with the following results:

	Dry matter Per Cent.	Per Cent. on dry matter			Ratio S: P
		Ash	Sulphur	Phosphorus	
Whole grain	87·1	1·92	0·161	0·476	0·338
Bran	88·37	7·19	0·123	1·368	0·090
Sharps	88·78	6·93	0·131	1·485	0·099
Flour (82 per cent. extraction)	87·27	0·72	0·190	0·183	1·039
Germ	87·42	5·55	0·231	1·298	0·178
Gluten: Whole	97·17	0·94	0·926	0·328	2·824
Gluten: Sol. in 70 per cent. alcohol	—	—	0·349	0·505	0·691
Gluten: Insol. in 70 per cent. alcohol	—	—	1·002	0·304	3·296

The phosphorus in gluten appears to exist, partly at least, in organic combination, possibly in a form similar to lecithin. T. H. P.

Determination of Nitrogen in Yeast and Brewing Materials. J. S. Ford, A. Tait, L. Fletcher, J. Spiers and W. J. Mitchell. (*J. Inst. Brewing*, **1933, 39**, 472–486.)—The recent criticisms and modifications of the Kjeldahl and Kjeldahl-Gunning methods (*cf.* especially Christensen and Fulmer, *Plant Physiol.* 1927, **2**, 455; Thorne, ANALYST, 1932, **57**, 182; and Case and Price, *J. Inst. Brewing*, 1933, **39**, 35) have cast doubt on many of the results obtained in the past in nitrogen determinations, particularly in yeast. The authors now show that, assuming the precautions described by them (*infra*) are taken, the original method and the Gunning, Christensen-Fulmer and Lundin-Ellburg (*Woch. Brau.*, 1929, **133**, 147) modifications, as well as ter Meulen's hydrogenation method (ANALYST, 1932, **57**, 524), give identical results for brewing materials. Excerpts from Kjeldahl's rather inaccessible original paper (*Medd. Carlsberg Lab.*, 1883, **2**, 1) are included, to illustrate the importance of adhering to details of his technique. Potassium permanganate should be used even if a catalyst is employed, in order to save time and to ensure complete oxidation, for a clear solution is not necessarily completely oxidised. Contrary to the conclusions of previous workers (*cf.* Thorne, and Case and Price, *loc. cit.*), it was found that no optimum exists for the amount of hydrogen peroxide required for the Christensen-Fulmer method, and also that the results are independent of the volume of acid used, so long as sufficient is taken. The only exception to the above statement encountered during determinations of nitrogen in various ring compounds, in complex substances, and in barleys, malts, worts and yeasts of various origins, was with alkaloids; in the presence of nitrates, also, uncertain results may be obtained, and it is therefore advisable to remove them or to modify them so that they are included in the determination. The hydrogenation method may give low results if steps are not taken to ensure the presence in the hydrogen of sufficient water-vapour to decompose the traces of nitrides formed. The following are the more important details of the actual technique:—*Kjeldahl Method with Copper Sulphate.*—The anhydrous copper sulphate (0·2 grm.) and 20 c.c. of acid should be taken for 0·2 to 0·3 grm. of dried yeast, 1·5 grm. of barley or malt, or 20 to 25 c.c. of wort. When the solution is clear, the flame should be removed and solid potassium permanganate immediately added, a little at a time, until a permanent green colour indicates an excess; according to Kjeldahl, further boiling at this stage gives low results, and 5 to 10 minutes over a small flame should suffice. *Kjeldahl-Gunning Method.*—Twenty c.c. of acid, 10 grms. of potassium sulphate, and 0·2 grm. of anhydrous copper sulphate are boiled with the sample for at least 2 hours after the mixture has become clear, potassium permanganate being then added as before; this is considered the most reliable of all the methods investigated. *Kjeldahl-Lundin-Ellburg Method.*—To 1 grm. of yeast in a 500-c.c. round-bottomed flask are added, in the following order, a copper spiral (approx. 0·5 grm., made from electrolytic copper), 3 glass beads, 10 c.c. of 90- to 100-volume hydrogen peroxide, and 10 c.c. of a mixture containing 3 parts of concentrated sulphuric acid and 2 parts of 85 per cent. phosphoric acid. The action should be gentle at first, being stimulated by heat or restrained by cooling according to circumstances, and, when the solution is clear, it is heated until evolution of dense white fumes has practically ceased. The burner is then removed, 7 grms. of potassium sulphate are added,

and boiling is renewed until the liquid is clear, the neck of the flask being closed by means of a "pear" stopper. After 1 minute the solution is diluted with water (drop by drop at first) to 120 c.c., and the distillation is then carried out in the usual way; full details are given of what the authors consider to be the best type of apparatus and technique. Yeast is best sampled by taking 50 c.c. of a suspension of 20 grms. of yeast in 1 litre of water. Dried yeast should be ground so as to pass a hair-sieve, a known amount being then weighed into a tared nitrogen-free rice-paper cachet, which is placed in an oven in order to obtain the moisture-content of the yeast, and is finally digested in the acid with the yeast. J. G.

Identification of Wine Vinegars, Spirit Vinegars and Artificial Vinegars. J. J. Dingemans. (*Ann. Falsif.*, 1933, **26**, 346–348.)—The identification of vinegars derived from fruit is based on the presence of methyl-acetol or carbinol formed in the course of fermentation. In the official Dutch method 50 c.c. of the vinegar are mixed with ferric chloride and slowly distilled, with the object of forming diacetyl by oxidation. The distillate is made alkaline with ammonia and treated with hydroxylamine acidified with nitric acid, so as to form dimethylglyoxime, and this is identified by the addition of nickel chloride ($NiCl_2$), which gives the well-known red precipitate of dimethylglyoxime nickel. If Reiff's method (ANALYST, 1925, **50**, 191) of detecting methyl-acetol in a vinegar gives a negative result, Schiff's reagent should be used. If the result is doubtful, Pratolongo's method of determining the iodine value may be applied, but this can only be done successfully with white vinegars, since the presence of caramel fixes the iodine. For coloured samples the following method is recommended:—To 10 c.c. of the vinegar are added 1 c.c. of phosphoric acid and 1 c.c. of 3 per cent. potassium permanganate solution, and the mixture is allowed to stand for 10 minutes. Rapid decolorisation of the permanganate occurs with wine vinegars; it is slower with spirit vinegars, and is negligible with artificial vinegars. On the further addition of 1 c.c. of saturated oxalic acid solution, 1 c.c. of 4 *N* sulphuric acid followed after a short interval by 1 c.c. of Schiff's reagent, the rapid formation of an intense red-violet colour is characteristic of wine vinegars, a pale violet of spirit vinegars, and the absence of colour of artificial vinegars. The formation, after some time, of a pale brown colour is due to the presence of caramel.

D. G. H.

Physico-chemical Characteristics of Egg-yolk Oil, and its Solubility in Ethyl Alcohol. G. Vita and L. Bracaloni. (*J. Pharm. Chim.*, 1933, **125**, 104–108.)—Egg-yolk oil, which had been purified by three extractions with ethyl alcohol at 95° C., and filtered at 70°–80° C., had the following characteristics:—Colour, orange-yellow; sp.gr. at 15° C. (Westphal), 0·98; m.pt., 16°–18° C.; solidification pt., 16°–17° C.; butyro-refractometer reading (Zeiss) at 25° C., 60·2°; saponification value, 199·5 to 200·5; iodine value, 69·8–70·3; m.pt. of fatty acids, 36°–38° C. Differences in analytical data reported by various authors are, at least in part, accounted for by differences in composition of the egg, largely due to the various methods of feeding the fowls, and also to the different methods used for the extraction and purification of the oil. The solubility of the oil in ethyl alcohol (the solvent most commonly used in the preparation of extract of egg) was determined

for 9 samples of alcohol at strengths ranging from 60 to 99 per cent., and at the temperatures of – 4° C., + 15° C., and + 37° C. It was found that with strong alcohol (90 to 99 per cent.) temperature greatly influenced solubility, but as the strength dropped this influence diminished; *e.g.* with 60 per cent. alcohol, at –4° C. 0·016 grm. of oil was soluble in 100 c.c.; at +15° C. 0·014 grm.; and at 37° C., 0·038 grm., whilst with 99 per cent. alcohol, the amount dissolved at –4° C. was 0·78 grm.; at 15° C., 1·63 grm.; and at 37° C., 3·24 grms. D. G. H.

Hazelnut (Filbert) Oil. H. A. Schuette and C. Y. Chang. (*J. Amer. Chem. Soc.*, 1933, 55, 3333–3335.)—Fresh imported Italian filberts (*Corylus avellana* L.) yielded, on expression, approximately 51 per cent. of a lemon-yellow oil, and a further 15·6 per cent. of golden-yellow oil on extraction with petroleum spirit. The two oils (both of mild taste) had the following characteristics:—Sp.gr. at 20°/20° C., 0·9144 and 0·9150; $n_D^{20°}$C. 1·4698 and 1·4700; saponification value, 191·2 and 190·2; iodine value (Hanus), 84·70 and 85·48; thiocyanogen value, 82·09 and 81·37; Reichert-Meissl value, 2·73 and 3·33; Polenske value, 0·57 and 0·71; acetyl value, 2·65 and 3·24; free fatty acids (as oleic acid), 0·15 and 0·32 per cent.; soluble acids (as butyric acid), trace and 0·02 per cent. Insoluble acids: Hehner value, 95·44 and 94·90; saturated acids (corr.), 4·87 and 5·20 per cent.; unsaturated acids (corr.), 90·97 and 91·45, with thiocyanogen value 86·82 and 89·22; saponification value, 192·1 and 194·6; iodine value (Hanus), 89·70 and 90·43; unsaponifiable matter, 0·55 and 0·50 per cent. The unsaturated acids gave no deposit of hexabromide from ether at – 10° C. (absence of linolenic acid). The unsaturated acid fractions of the two oils were calculated by the method of Kaufmann to have the following compositions:—oleic acid, 88·10 and 86·87, and linolic acid, 2·87 and 4·58 per cent. The saturated acids consisted of myristic acid (0·22 and 0·46), palmitic (3·06 and 3·61), and stearic acid (1·59 and 1·13 per cent.). The expressed oil and that recoverable by subsequent extraction of the residual pulp differ in flavour, colour and composition, but the differences in composition are quantitative rather than qualitative. D. G. H.

Fat from the Seeds of *Vateria Indica* Linn. S. V. Puntambekar and S. Krishna. (*J. Indian Chem. Soc.*, 1933, 10, 203–211.)—Dried and powdered kernels from the seeds of the evergreen tree *Vateria indica*, N.O. *Dipterocarpaea*, obtained from Mangalore, yielded, on expression, 14 per cent., and, on further extraction with petroleum spirit, another 8 per cent. of a pale yellow tallow-like fat, fading to white on standing, with a corresponding fall in iodine value. The fat had: m.pt., 40° C.; sp.gr. at 20° C., 0·9120; $n_D^{25°}$C., 1·4556; saponification value, 190·4; iodine value (Hanus), 40·0; acetyl value, 2·45; Hehner value, 97·6; acid value, 1·4; and unsaponifiable matter, 0·8 per cent. The stearic acid was separated from the mixed fatty acids by repeated crystallisation, and the remaining acids were treated three times by Twitchell's process, 61 per cent. of saturated, and 39 per cent. of unsaturated acids being thus obtained. The solid acids consisted mainly of stearic acid with small amounts of myristic acid (not isolated) and lignoceric acid (isolated). Palmitic and arachidic acids were not found. The fatty acids were calculated to have the following composition:—Acid taken as myristic, 1·16; stearic, 58·76;

lignoceric, 0·62; elaidic (*iso*-oleic?), 13·55; oleic and elaidic (*iso*-oleic?), 18·66; dihydroxystearic (as oleic), 3·55; isomeric dihydroxystearic (as oleic), 3·70 per cent. D. G. H.

Determination of Chlorogenic Acid in Raw and Roasted Coffee. C. Griebel. (*Chem.-Ztg.*, 1933, **57**, 353–354.)—For the determination of the chlorogenic acid use is made of the method and conditions laid down by Hoepfner (ANALYST, 1933, 100), except that removal of fat from the coffee is effected by means of petroleum spirit instead of acetone. The percentages of chlorogenic acid (on dry matter) found in three samples of coffee, in the raw state and after treatment in various ways, are:

	Raw coffee	After 2 hrs. treatment with steam at 2 atm.	Roasted coffee	
			Not steamed	Steamed for 2 hrs.
African ..	7·93	8·10	5·94	5·91
Brazil 1 ..	6·66	6·69	4·33	5·29
„ 2 ..	6·45	6·47	3·10	4·45

Contrary to Hoepfner's observation, these results indicate that treatment of coffee with steam effects no diminution in the content of chlorogenic acid, but that such diminution does result from roasting alone. The actual proportions of chlorogenic acid found in raw coffees correspond with those found by Hoepfner. The above method requires a suitable colorimeter or spectro-photometer, but, in absence of these, sufficiently accurate results may be obtained by hydrolysing the chlorogenic acid with alkali and titrating the caffeic acid formed. Two grms. of the raw coffee are de-fatted with petroleum spirit and then boiled in a 200-c.c. flask, first with 40 c.c., and afterwards with four 20-c.c. quantities of water, a small flame being used and the boiling maintained for 15 minutes in each case. The total liquid is made up to 100 c.c. and filtered, 50 c.c. of the filtrate being evaporated to dryness in a glass basin of about 30 c.c. capacity. The residue is taken up in 1 c.c. of water, 0·5 c.c. of 32 per cent. sodium hydroxide solution is added, and the solution is stirred to dissolve any remaining solid. After standing for 15 minutes the liquid is acidified with dilute sulphuric acid and shaken in a separating funnel with three quantities of ether, each the fourfold volume of the acidified liquid. The combined ethereal extracts are dried with sodium sulphate (which must be afterwards washed out) and evaporated to dryness in a wide-necked flask. The residue is dried at 100° C. until odourless, dissolved in hot water and titrated with 0·1 *N* sodium hydroxide solution, with the help of sensitive litmus paper; 1 c.c. of the alkali ≡ 0·018 grm. of caffeic acid, and chlorogenic acid yields, on hydrolysis, 50·8 per cent. of its weight of caffeic acid. T. H. P.

Determination of Hexamethylenetetramine in Pharmaceutical Preparations. E. Schelek and V. Gervay. (*Z. anal. Chem.*, 1933, **95**, 406–417.)—According to Kolthoff (*Die Massanalyse*, 1928, II, 128), hexamethylenetetramine can be determined with sufficient accuracy by titration with *N* hydrochloric acid, if a comparison solution is used, but most of the methods suggested are based on decomposition of the compound with acid and subsequent determination of either

the ammonia or the formaldehyde thus liberated. For pharmaceutical preparations the authors consider it best to determine the formaldehyde, although it must be borne in mind that such preparations often contain sugars and, during the heating with sulphuric acid, these yield volatile, highly-reducing decomposition products. Experiment shows that the formaldehyde can be separated quantitatively from the acid solution only by distilling until sulphur trioxide vapours appear, diluting the cooled residue with water, and repeating the distillation. The formaldehyde may be determined by means of its instantaneous reaction, in neutral or alkaline solution, with potassium cyanide, giving the potassium compound of glycollic acid nitrile, which gradually decomposes into potassium glycollate and ammonia. Condensation of the cyanide with other aldehydes is so slow that it may be neglected.

Two methods are described. If 0·1 *N* solutions are to be used, or if substances such as piperazine, salicylic acid, or phenylcinchonic salts, which interfere with the determination of the formaldehyde, are present, the aldehyde must be separated by distillation. For this purpose use is made of the apparatus used for determining boric acid (ANALYST, 1932, **57**, 335) and nitroglycerin (*Pharm. Zentralh.*, 1932, **73**, 673, 692). As much of the finely powdered sample as corresponds with 0·04 grm. (micro method) or 0·4 grm. (macro method) of hexamethylenetetramine is dissolved in warm water, cooled, made up to 100 c.c., and, if necessary, filtered through a pleated filter. The first portion of the filtrate is discarded, 10 c.c. of the remainder being placed in the 100-c.c. flask of the apparatus and there mixed with 20 c.c. of water and 10 c.c. of 50 per cent. sulphuric acid. The larger flask (250 c.c.) is used if the substance contains much sugar or other strongly frothing matter. The ground joint of the flask is moistened with concentrated sulphuric acid and the apparatus assembled. A 100-c.c. measuring flask, containing a few c.c. of water, beneath which the end of the condenser tube dips, serves as receiver. The distillation is started carefully with a small flame, and is continued until sulphuric acid vapours appear in the neck of the distillation flask. The cooled residue is diluted with 25 to 30 c.c. of water, added through the fitted funnel, and the distillation is repeated until sulphuric acid vapours are again observed; a second repetition of this procedure is made. The receiver is then lowered, the condenser tube being rinsed with water into the receiver, and the distillate made distinctly alkaline (towards methyl red) with *N* sodium hydroxide and diluted to 100 c.c.

To determine the formaldehyde, 30 c.c. of this distillate are placed, with 5 c.c. of 0·02 *N* or 0·2 *N* (according to the amount of the aldehyde) potassium cyanide solution, in a 100-c.c. Erlenmeyer flask with a closely-fitting glass stopper. After the lapse of 15 minutes the solution is acidified with 5 c.c. of 20 per cent. phosphoric acid solution and treated, dropwise, with fresh saturated bromine water until a yellow colour persists. The liquid is then well shaken with 1 to 2 c.c. of 5 per cent. phenol solution to remove the excess of bromine, and, after 5 minutes, is mixed with 0·5 grm. of potassium iodide. When this has acted for 30 minutes in the dark, the separated iodine is determined by titration with 0·01 *N* or 0·1 *N* sodium thiosulphate solution. The titre of the potassium cyanide solution (5 c.c. taken) is ascertained by means of a blank test with 30 c.c. of distilled water, the difference between the volumes of thiosulphate used in the two titrations giving the potassium

cyanide used to fix the formaldehyde: 1 c.c. of 0·1 *N* thiosulphate ≡ 1·16771 mgrm. of $(CH_2)_6N_4$.

The second method, which is a micro-method, and is applicable only in absence of the disturbing substances referred to above, is as follows: A portion of the fine material corresponding with about 0·01 grm. of hexamethylenetetramine is dissolved, and the solution is made up to 100 c.c. Of this solution, filtered through a folded filter if necessary, 10 c.c. are transferred to a 100-c.c. glass-stoppered measuring flask and acidified with 2 drops of 50 per cent. sulphuric acid. The flask is heated on a water-bath and stoppered. After 10 to 20 minutes it is cooled and the contents are made just alkaline with *N* sodium hydroxide solution (to methyl red) and mixed with 5 c.c. of 0·02 *N* potassium cyanide solution. In 10 minutes' time the excess of the cyanide is determined iodimetrically, as described above. If salicylic acid is present, it may be removed by a double distillation. The first distillate is made exactly neutral to phenolphthalein with 0·1 *N* sodium hydroxide solution and redistilled before being treated with potassium cyanide.

T. H. P.

Extraction of Capsaicin and its Determination in Capsicum Fruit and Oleoresin. L. F. Tice. (*Amer. J. Pharm.*, 1933, **105**, 320–325.)—Approximately 100 grms. of oleoresin of capsicum (Mombasa) are placed in a separating funnel and twice the volume of petroleum oil (heavy liquid petrolatum) are added. After the liquids have been thoroughly mixed and shaken, three extractions are made with 200-c.c. portions of 57 per cent. alcohol, the mixed extracts are treated with 100 c.c. of the petroleum oil, and, after shaking, the separated alcoholic layer is drawn off. The alcohol is distilled, and the cooled aqueous liquid is extracted with ether, sodium chloride being used to prevent emulsification. After evaporation of the ether, 4 grms. of lithium hydroxide (carbonate-free) and 200 c.c. of water are added to the oily residue, and the mixture is boiled for 10 minutes, with occasional stirring, and allowed to stand overnight. Carbon dioxide is then passed in intermittently for 2 hours, water being added if the liquid is too thick, and the mixture is again left overnight. It is then filtered, and the precipitate is washed with water and dried at a low temperature, after which it is boiled with 500 c.c. of petroleum spirit for 15 to 20 minutes, the spirit is poured while hot through a filter paper, and the filtrate is left overnight to crystallise in a sub-zero refrigerator. Any undissolved material is kept for subsequent extraction with petroleum spirit. The chilled petroleum spirit is rapidly filtered, and the crystals are dried and placed in a closely-stoppered bottle. If several extractions of the precipitate are made, at least 5 grms. of capsaicin should be obtained; this gives all the recorded identity tests, and melts at 64 C°. For the colorimetric assay a modification of Fodor's method (*Z. Unters. Lebensm.*, Sept. 26, 1930) is used. This is based on the reaction of vanadium oxytrichloride with capsaicin, to produce an intense blue compound, vanadyl capsaicin ($C_{18}H_{26}NO_3.VOCl_2$). A representative sample of capsicum is dried overnight in a desiccator, and a 2 per cent., w/v, extraction is made by macerating it for 30 to 60 minutes with dry acetone (if the oleoresin is being used a 0·2 per cent. solution in acetone is made). A 0·02 per cent. solution of the active principle in dry acetone is now prepared, and is coloured by extracting

sufficient capsaicin-free paprika (0·1 to 0·2 per cent.) to give a colour approximating to that of the 2 per cent. extract under examination. Standard tubes are prepared by diluting to 5 c.c., with coloured acetone, the correct quantity of the 0·02 per cent. solution of capsaicin in coloured alcohol. Thus 1·5 c.c. of 0·02 per cent. capsaicin solution, and 3·5 c.c. of coloured acetone give a standard with 0·006 per cent. of capsaicin; 2·0 c.c. of 0·02 per cent. capsaicin solution and 3·0 c.c. of coloured acetone are equivalent to 0·008 per cent. of capsaicin, and so on. The standards are placed in sequence, followed by tubes containing the unknown solutions. One drop of a 1 per cent. solution by volume of vanadium oxytrichloride is added to each of the standards for every thousandth of a per cent. of capsaicin present, and immediately after to the unknown solutions, drop by drop, until no deepening in blue colour is noticed, but not in sufficient quantity to give a green tinge, which would make matching impossible. Since the colour slowly fades, the additions must be made quickly. The tube containing the unknown solution with the greatest depth of blue is matched with the standard of the nearest colour depth, preferably by looking down through the tubes at a source of diffused illumination. The capsicum samples examined contained from 0·1 to 1·0 per cent. of capsaicin, and Mombasa capsicum (both the drug and the oleoresin prepared from it) was unquestionably the best variety. The placenta contains the preponderance of active principle; the cortex and seeds practically none. It is suggested that the vanadium oxytrichloride reaction might be utilised for the colorimetric determination of certain phenols with which it also reacts.

D. G. H.

Determination of Coumarin and Melilotic Acid in *Melilotus Officinalis*. Sophia J. Kanewskaja and Alexandra M. Fedorowa. (*Z. anal. Chem.*, **1933**, **93**, 176–180.)—The method described is based on the fact that, when coumarin is treated with boiling alkali solution, its lactone ring is opened and salts of coumaric acid pass into solution, from which they cannot be extracted with ether. Such salts are decomposed by acids, even carbonic acid, the unstable coumaric acid thus liberated reverting to coumarin. Thus, coumarin may be separated from neutral ether-soluble substances accompanying it in solution, by boiling with alkali, cooling, extracting with ether, acidifying the residual liquid and extracting the re-formed coumarin with ether. The accuracy of a procedure based on the above considerations is shown by the results obtained with pure coumarin, both alone and when mixed with melilotic acid.

To determine these two substances in *Melilotus officinalis*, 20 grms. of the air-dried, finely powdered leaves are extracted for 12 hours with ether in an efficient Soxhlet apparatus. After the ether has been distilled from the extract, the viscous dark green residue in the flask is heated to boiling for 5 minutes with 25 c.c. of water under a reflux condenser. The solution obtained is filtered through a moist filter (7 cm.), the undissolved matter being left in the flask; this operation is repeated four times. The resulting green aqueous solution, containing the coumarin, melilotic acid, and a small amount of coloured substances, is heated to boiling and treated with 20 c.c. of boiling 10 per cent. sodium or potassium hydroxide solution, and, when cold, is extracted three or four times with 50-c.c.

quantities of ether; the aqueous solution becomes colourless and the ether green. The aqueous liquid is made acid to Congo red by addition of 20 per cent. sulphuric acid, the coumarin and melilotic acid being thrown out. To separate the two, the solution is made alkaline with sodium hydroxide, and extracted four or five times with ether, which is filtered through a small filter. The combined ethereal solutions are evaporated to a small volume, the residue, together with three or four ether rinsings of the flask, being transferred to a weighed crystallising dish (7 cm. wide). After the ether has evaporated, the dish is left over sulphuric acid in a desiccator until constant in weight; this gives the coumarin. The alkaline solution, from which the coumarin was extracted with ether, is acidified with 20 per cent. sulphuric acid solution and extracted with four or five 50-c.c. portions of ether. The subsequent operations are carried out as in the determination of the coumarin. The crystalline residue with a characteristic odour of honey consists of the melilotic acid.

With 14 samples of *Melilotus officinalis* of various origins and ages, the following results were obtained: Percentage of coumarin in leaves, 0·098 to 0·72; in stems, 0·1 to 1·35. Percentage of melilotic acid in leaves, 0·99 to 2·9; in stems, 0·4 to 1·6. T. H. P.

Helch's Reaction for Pilocarpine. F. Bredebach. (*Apoth.-Ztg.*, 1933, **49**, 723; *Pharm. J.*, 1933, **131**, 298.)—In Helch's test for pilocarpine the solution of the alkaloid is treated with hydrogen peroxide and potassium dichromate solution and shaken with benzene. In the presence of pilocarpine the benzene layer becomes blue, and the reaction cannot be confused with the formation of perchromic acid, which is insoluble in benzene. The blue compound, which gave the reaction of a perchromate, was dissolved in dilute sulphuric acid and alcohol, the solution was treated with barium carbonate and filtered, and the filtrate was concentrated by evaporation and extracted with chloroform. The residue from the chloroform extract consisted of pilocarpine, showing that the blue compound is pilocarpine perchromate.

Polarimetric Determination of Nicotine in Tobacco and Tobacco Smoke. E. Toole. (*Z. anal. Chem.*, 1933, **93**, 188–194.)—Pfyl and Schmitt (ANALYST, 1927, **52**, 728) regard the polarimetric determination of nicotine in tobacco as open to objection, owing to possible racemisation of the nicotine in tobaccos which have been "de-nicotinised" by heating. This possibility has been tested by the author, who finds that no racemisation occurs either when the tobacco is heated for 1 hour at 160° C.—the maximum heat-treatment permissible if the quality is not to be endangered—or during the smoking of the tobacco.

Examination of Pfyl and Schmitt's method for tobacco smoke shows that, if the nicotine is precipitated directly with picric acid from the smoke solutions obtained, unsatisfactory results are often obtained, as the crystallisation of the nicotine dipicrate is retarded by oily and resinous surface-active components to such an extent that when only small amounts of nicotine are present, none may be found. The following modifications of this method of investigating tobacco smoke are hence suggested:—The 30 c.c. of chloroform and 30 c.c. of N sulphuric acid in the first absorption flask are replaced by 50 c.c. of 96 per cent. alcohol and

2 to 4 c.c. of 10 per cent. sulphuric acid (for 5 to 10 grms. of tobacco). The cigarettes or cigars are to be smoked continuously and completely, the duration of the burning being kept as nearly constant as possible. The final absorption flask should be tested with silicotungstic acid to ascertain if the nicotine is being completely absorbed. At the end of the test the washing flasks, connections thimbles, etc., should be thoroughly rinsed with hot, slightly acidified alcohol, this being mixed with the liquid from the absorption flasks and the whole made up with water to a definite volume at least five times that of the alcohol used. This solution is passed through a dry filter to remove the bulk of the tarry products. From an aliquot part of the acid filtrate, containing about 0·05 to 0·1 grm. of nicotine, alcohol and ethereal oils are driven off in steam; 200 c.c. of distillate are taken off. The residue, having one-half or one-third of the original volume, is made neutral to litmus by addition of sodium hydroxide solution, treated with magnesium oxide and sodium chloride, and steam-distilled into 0·1 *N* hydrochloric acid until a little of the distillate gives no turbidity with silicotungstic acid; from 150 to 200 c.c. of distillate are thus collected. This liquid is mixed with one-third of its volume of saturated picric acid solution and left overnight, after which it is filtered through asbestos and the precipitate washed. To prevent adhesion of the picrate, the precipitation flask and the filter should be previously freed from traces of fat by means of chromic-sulphuric acid mixture.

The subsequent treatment applies also to the picrate precipitate obtained by Pfyl and Schmitt's method from tobacco itself. The precipitate is washed with the least possible amount of water into a 100-c.c. Erlenmeyer flask and titrated with 0·1 *N* sodium hydroxide solution (phenolphthalein). The liquid is then shaken with 10 c.c. of toluene, and the titration continued. An amount of the sodium hydroxide solution equal to that used, less what corresponds with the carbon dioxide of the water used (determined by a blank titration), is added to the liquid. The whole is shaken for 30 seconds in a separating funnel (12 × 3 cm.) and left for a time, the emulsion formed being destroyed by gentle swirling and by stirring with a fine glass rod. The aqueous solution is run off and the toluene solution of nicotine is transferred to a 100-c.c. Erlenmeyer flask and stoppered. The aqueous layer is again shaken with 0·2 c.c. of 0·1 *N* sodium hydroxide solution and 10 c.c. of toluene, and the separated toluene extract is added to the first (solution I). Two further treatments of the aqueous layer with 10-c.c. portions of toluene are carried out, the shaking being continued for 4 to 5, and 13 minutes, respectively; these, together, give solution II. Solutions I and II are filtered separately through dry covered filters and polarised in a 10-dm. tube at 16 to 17° C. in sodium light. For solutions of 0·2, 0·133, 0·1, 0·067, and 0·033 grm. of pure nicotine in 10 c.c. of toluene, the mean readings found were 3·44 ± 0·04°, 2·35 ± 0·03°, 1·76 ± 0·04°, 1·12 ± 0·03°, and 0·50 ± 0·04°.

Five c.c. of each solution (I and II) are shaken, separately, in a stoppered 100-c.c. Erlenmeyer flask for a minute with a drop of methyl red and with 0·01 *N* hydrochloric acid (about 5 c.c. in excess). The toluene is then boiled away and the excess of acid titrated with 0·01 sodium hydroxide; 5 c.c. of standard nicotine solution (0·033 grm. per 20 c.c.) are similarly treated. Results thus obtained were satisfactory (*cf.* Pyriki, ANALYST, 1933, 487). T. H. P.

Keeping Properties of Liquor Arsenicalis. E. M. Smelt. (*Pharm. J.*, 1933, **131**, 134–135.)—The occurrence of moulds and deposits containing arsenic trioxide in some specimens of Liquor Arsenicalis B.P. 1932, kept in completely filled unopened bottles, has been confirmed. The suggested use of sodium hydroxide instead of potassium hydroxide was found to encourage rather than prevent the growth of moulds. Contrary to the experience of Rae (ANALYST, 1933, 357), contamination with traces of nitrate did not increase the tendency of moulds to grow. Apart from the use of preservatives, most of which are unsuitable for the preparation, the growth of moulds could be inhibited by adjusting the p_H of the solution to 2·0 or to 8·0. The limits of p_H beyond which the formation of arsenic trioxide crystals would be prevented were considered to be 3·0 and 9·0. An alkaline solution is undesirable on account of its incompatibility with solution of strychnine hydrochloride, and an acid solution is to be preferred.

Detection and Differentiation of Phosphites and Hypophosphites in the presence of each other. D. Raquet and P. Pinte. (*J. Pharm. Chim.*, 1933, **125**, 89–93.)—In the absence of substances reacting with iodine in alkaline or acid medium, phosphites may be detected by the addition of a little sodium acetate and a few drops of approximately 0·1 *N* iodine solution to a 10 per cent. solution of the salt, when decolorisation will occur. If the sodium acetate is replaced by 20 drops of concentrated sulphuric acid, decolorisation denotes the presence of a hypophosphite, and a mixture of phosphite and hypophosphite will cause decolorisation in either case. As little as 0·001 grm. of phosphite or hypophosphite may thus be detected, and between 1 part in 400 and 1 in 500 of hypophosphite in a phosphite, or *vice-versa*. With very dilute solutions only 1 drop of iodine solution should be used, and the decolorisation may not occur until after 15 minutes. D. G. H.

Biochemical

Uricase and its Action. VI. Distribution in Various Animals. R. Truszkowski and C. Goldmanówna. (*Biochem. J.*, 1933, **27**, 612–614.)—For the first time a systematic study has been made of the distribution of uricase in the individual organs and tissues of various animals. In most cases 2 grms. of fresh organ were shaken for 60 minutes with 20 c.c. of 0·025 to 0·05 per cent. uric acid (as lithium salt, at p_H8) in the presence of 1 c.c. of toluene, and uric acid was determined colorimetrically by the method of Folin and Denis (*cf.* ANALYST, 1923, **48**, 79). The results, calculated as mgrms. of uric acid oxidised per grm. of fresh tissue, are tabulated, and indicate that the sole organs possessed of uricolytic activity in widely distributed species of animals are the liver or kidneys, or both. Uricase was present in the liver of every animal examined. It was also present in the kidneys of oxen, pigs, dogs, rats and frogs, but it was absent from the kidneys of the horse, sheep, cat, rabbit, guinea-pig, mouse, hedgehog, bat, carp and crayfish, and from all organs other than the liver and kidneys of all animals examined. In the ox, uricolysis is performed chiefly by the kidney; in the frog, the activity of the kidney is approximately equal to that of the liver; in dogs,

pigs and rats the kidney tissue has comparatively little activity. In dogs, the activity found for liver and kidney tissues varied considerably with the breed and, possibly, with the individual. In a female rabbit the foetal livers had the same uricolytic activity as the maternal liver. No connection appeared to exist between the distribution of uricase and the phylogenetic relationships of the animals examined. P. H. P.

Presence of Allantoic Acid in Fungi. R. Fosse and A. Brunel. (*Compt. rend.*, 1933, **197**, 288–290.)—Allantoic acid occurs, not only in phanerogams, but also in fungi. After being defecated and heated, the expressed juice of many *Basidiomycetes* gives with phenylhydrazine the colour reaction of glyoxylic acid, formed together with urea by hydrolysis of the allantoic acid. This acid may be identified as its dixanthyl derivative, which is isolated as follows:—The ripe fungus is rapidly dried in a vacuum over calcium chloride, 20 grms. of the dried material being ground and the powder left in contact with ice-water (200 c.c.) for an hour. The mass is then centrifuged and washed, the liquid being made up to 200 c.c. and defecated with *N*-silver nitrate solution (40 c.c.). The solution is mixed with mercuric acetate solution, and the mixture is left overnight in an ice-chest for the allantoic acid compound to precipitate. The deposit is separated, washed, suspended in ice-water and treated with hydrogen sulphide. After removal of the mercuric and hydrogen sulphides the liquid is made alkaline with sodium hydroxide and then treated with its own volume of acetic acid and one-fortieth of its volume of a methyl alcohol solution of xanthydrol (1: 10). After remaining for 4 hours in the ice-chest the precipitate formed is separated, washed with dilute acetic acid (1: 2) and afterwards with water, and purified from its pyridine solution. It is dried at 100° C., and its nitrogen-content (10·44 per cent.) is determined.

The proportions of allantoic acid in a number of fungi were determined spectrophotometrically and found to vary widely. Certain species contain only about 0·01 per cent. on the dry matter, but *Leucocoprinus cæpestipes* contains 0·609 and *Rhodophyllus solsticialis* 0·672 per cent. The proportion present increases greatly during the development of the fungus. T. H. P.

Detection of Quinine in Urine by the Erythroquinine Reaction. R. Monnet. (*J. Pharm. Chim.*, 1933, **125**, 94–96.)—The quinine is first extracted from 20 c.c. of the urine (which has been rendered alkaline with ammonia) with 5 c.c. of chloroform, and 2 c.c. of the chloroform solution are shaken with 5 c.c. of 1 per cent. acetic acid. If sufficient quinine is present, a blue fluorescence is observed. Saturated bromine water, diluted six times, is then added, drop by drop and with shaking after each addition, until there is a persistent pale yellow colour. This is followed by 10 per cent. potassium ferrocyanide solution, one drop for every five drops of bromine solution used, and, finally, the mixture is rendered faintly alkaline with 10 per cent. ammonium hydroxide. On shaking, the chloroform separates as a pink or red layer according to the quantity of quinine present, and the colour is stable for 2 to 3 hours. By this reaction 0·1 mgrm. of quinine in 10 c.c. of urine could be detected and colorimetrically determined, and the elimination of a 0·25 grm. tablet of quinine sulphate was followed up to the

60th hour. Neither antipyrin nor pyramidon is dissolved by the chloroform in sufficient quantity to affect the reaction, and no other substances administered with quinine have been found to interfere. D. G. H.

Sullivan's Reaction for the Quantitative Determination of Cysteine and Cystine. J. W. H. Lugg. (*Biochem. J.*, 1933, **27**, 668–673.)—The colour test for cysteine described by Sullivan (*U.S. Pub. Health Reports*, 1926, **41**, 1030; 1929, **44**, 1421, 1599), depending upon the production of a red soluble complex of cysteine and sodium 1: 2-naphthoquinone-4-sulphonate, has been examined with the object of improving his procedure for the determination of cysteine and cystine in solutions containing these amino-acids. Sullivan's procedure consists essentially in allowing the cysteine to react with the reagent in alkaline solution. Subsequently sulphite and more alkali are added, and are followed, after the lapse of 10 to 30 minutes, by an alkaline solution of sodium hydrosulphite, after which addition the red colour due to cysteine is retained, whilst colours due to other amino-acids are changed to yellow. The addition of a small quantity of cyanide before the reagent is thought to "check oxidation" of the cysteine, and a little more after the hydrosulphite "stabilises" the colour. For cystine the solution is first treated with plenty of cyanide, and then the cysteine procedure is followed. With this method the author finds: (i) The depth of red colour is variable and far from proportional to the amount of cysteine or cystine present. (ii) Even when compared with a standard of nearly the same colour, the results of the unknown are often irregular. (iii) The presence of relatively considerable amounts of other amino-acids diminishes the amount of red colour due to cysteine or cystine, and the yellow colour due to the other amino-acids interferes when a pure cysteine or cystine standard is used for comparison. The diminution in red colour was found to be attributable in part to the buffering effects of the amino-acids present upon the p_H of the solution. Two directions in which the accuracy of the method might be improved were: (i) to maintain the same p_H in standard and assay, and (ii) to swamp both standard and assay with a considerable amount of amino-acid. It was found possible to effect both objects by the addition of glycine with appropriate amounts of alkali, and by this means, two of the most serious drawbacks to Sullivan's procedure (unreliability and lack of proportionality) were overcome. It was found that the reaction between the cystine and cyanide was the double decomposition: RSSR + NaCN—> RSNa + RSCN, which, under conditions that may be varied considerably, proceeds so nearly to completion that any deviation from it cannot be detected colorimetrically. A method has now been evolved, and is described in detail, which permits of the colorimetric determination of cysteine or cystine (to within 1 or 2 per cent.) in pure solution. The same method has been applied successfully to the determination of cystine in the presence of large quantities of other amino-acids and of the hydrolysis products of carbohydrates. Some possible sources of error are discussed. P. H. P.

Vitamin *A* and Carotene. X. The Relative Minimum Doses of Vitamin *A* and Carotene. T. Moore. (*Biochem. J.*, 1933, **27**, 898–902.)—It is briefly shown that the minimum doses quoted by various workers both for vitamin *A*

and carotene vary over a wide range, and thus any attempt to deduce a ratio comparing the activities of the two substances from published data collected at random must be almost meaningless. The biological activities of *B*-carotene and of a vitamin *A* concentrate, prepared from turbot-liver oil, have now been compared in parallel experiments on closely matched groups of rats. Charts show the results, and from them it is plain that *B*-carotene possesses biological activity equal to that of about the same weight of "pure" vitamin *A*, although the latter has a blue value some 10 to 20 times greater, *i.e.* the blue unit of carotene is equivalent to some 10 to 20 blue units of vitamin *A*. It is concluded, from calculations based on the amount of pure vitamin *A* presumed to be present in the concentrate, that, contrary to views widely held, carotene is utilised in the body as efficiently as preformed vitamin *A* at levels approaching the minimum dose. P. H. P.

Variations in the Quality of Butter, particularly in Relation to the Vitamin *A*, Carotene and Xanthophyll Contents as influenced by Feeding Artificially Dried Grass to Stall-Fed Cattle. A. E. Gillam, I. M. Heilbron, R. A. Morton, G. Bishop and J. C. Drummond. (*Biochem. J.*, 1933, **27**, 878–888.)—An experiment carried out in the winter of 1931–32 with four groups of cows was designed to measure the effects of two types of artificially dried grass, and of grass silage, on the quality of the resulting milk and butter in comparison with that produced on a normal winter ration. The values for the carotene, xanthophyll and vitamin *A* contents of the butters were determined spectroscopically for the whole period of the experiment. The results (given in tables and charts) show that for cows fed on normal winter rations of hay and concentrates, the carotene, xanthophyll and vitamin *A* values fall steadily during the winter and remain at a very low level until the cows go out to grass in the spring. The consumption of fresh grass then results in a very rapid rise of the quantities of all three substances present in butter. In the case of cows fed on artificially dried non-nitrogen-treated grass, the butters showed, very soon after the change over from the control diet, an increase in the content of the two carotenoids and of vitamin *A*, which was maintained until all the groups were again placed on the control diet, when the values dropped to the low control level. The results with the nitrogen-treated artificially dried grass were even better than with the non-nitrogen grass. Grass silage of moderate quality was found to be little superior to the normal winter ration in its effect on the colour and vitamin *A* of the butter. It may be concluded that the relatively high proportions of carotene, xanthophyll and vitamin *A* present in summer butter can be maintained during the winter period of stall feeding by the use of artificially dried grass. In an examination of the unsaponifiable matter of grass it has been found that the spectroscopic blue test with antimony trichloride gives higher values for both carotene and xanthophyll than does the direct absorption spectrum method (about 1·3 times as much for carotene and 2·2 times for xanthophyll). The discrepancies are being investigated further, but it is already possible finally to rule out the plausible suggestion that they are due to the presence in grass of the vitamin *A* of liver oils. The presence of ergosterol has been definitely established in the unsaponifiable matter of grass.

P. H. P.

Carotene Content, Vitamin *A* Potency, and Anti-oxidants of Butter-Fat. C. L. Shrewsbury and H. R. Kraybill. (*J. Biol. Chem.*, 1933, **101**, 701–709.)—Carotene cannot be determined satisfactorily in melted butter by direct comparison with a dichromate standard in a colorimeter, as the results are several times too high, and the colour intensity is several times greater than when the fat is dissolved in petroleum spirit. The petroleum spirit solution of carotene can be used for colorimetric determinations, with a reasonable degree of accuracy. Carotene may also be determined with considerable accuracy both in petroleum spirit solution and in butter-fat dissolved in petroleum spirit, by the spectrophotometric method. Removal of the colour of butter-fat with charcoal also removed the vitamin *A*. Experiments to determine whether the vitamin *A* activity of the butter sample could be attributed to carotene were not very conclusive, but it appears safe to conclude that an appreciable amount of the vitamin *A* activity may be due to its carotene content. The natural anti-oxidants, which protect the carotene in butter-fat from oxidation, are destroyed or removed by treatment with animal charcoal, and, if carotene is added to decolorised butter, the colour fades rapidly, whereas if it is added to untreated butter the colour remains unchanged. D. G. H.

Antiscorbutic Potency of Apples. VI. T. Wallace and S. S. Zilva. (*Biochem. J.*, 1933, **27**, 693–698.)—It has previously been shown that, whereas Bramley's Seedling apples are antiscorbutically more active than King Edward apples, both varieties being typical late culinary sorts, their nitrogen-content is definitely lower. Bracewell, Wallace and Zilva (*Biochem. J.*, 1931, **25**, 144) attempted to ascertain whether by changing the nitrogen-contents of fruits of these varieties their antiscorbutic activities could at the same time be influenced; they found that in the case of the King Edward variety the vitamin *C* content was indeed higher in the apples in which the nitrogen-content was lowered by cultural treatment, *i.e.* by the substitution of "grass" for arable culture, but, in the case of the Bramley's Seedling variety, the difference in the antiscorbutic potency between the high and low nitrogen apples was very much less marked. The experiments have been repeated and extended during the last three years. The nitrogen-contents of the two varieties previously used have been varied by two methods: (i) by the substitution of "grass" for arable culture, and (ii) by the operation of bark-ringing vigorous trees. In these two cases the "grass" and bark-ringing practices lower the nitrogen-contents of the fruits and at the same time usually increase the percentages of dry matter and total sugars, bark-ringing being generally more effective in increasing the latter two constituents. The results of the biological tests show consistently a higher antiscorbutic activity in apples in which the nitrogen is lowered by either of the two methods. This increased activity, although not so very marked in some Bramley's Seedling samples, falls definitely outside the limit of the experimental error of the prophylactic method in the other samples of this variety. The lowering of the nitrogen-content in the King Edward apples by cultural treatment or by ringing raised the vitamin *C* content of the fruit as much as 1·5 to 2 times. It is quite likely that the Bramley's Seedling variety, being antiscorbutically one of the most active, possesses

almost the maximum potency possible in the apple. The results obtained are definite enough, in the opinion of the authors, to support the view that in the case of apple varieties an inverse relationship exists between the nitrogen-content and the vitamin *C* activity; the inverse relationship is not, and would not be expected to be, strictly proportional. P. H. P.

Influence of Manuring on the Content of Vitamin *C* in Spinach. F. V. v. Hahn and J. Görbing. (*Z. Unters. Lebensm.*, 1933, **65**, 601–616.)—A large number of experiments on the prevention of scurvy in guinea-pigs on a diet free from vitamin *C* by spinach are described. The vitamin-content of spinach is found to vary greatly with the lime-content of the soil on which the plant is grown and with the character of the manuring. If a soil, rendered neutral by liming, is not fertilised with potash, phosphoric acid, and nitrogen, the resulting spinach is very low in vitamin-content, lack of one of these three components producing this effect. With balanced fertilising, however, the maximum amount of vitamin is attained. Not only unsuitable manuring, but also any departure from the normal of the conditions during growth, tends to diminish the vitamin-content. T. H. P.

Ascorbic Acid Content of the Adrenals and Livers of Different Animals. J. L. Svirbely. (*Biochem. J.*, 1933, **27**, 960–963.)—A study has been made of the reducing capacity, and hence of the ascorbic acid content, of the adrenals and livers of different animals under normal and varied experimental conditions. The results not only give an idea of the distribution of the acid, but at the same time form a test of the reliability of the method of determination if compared with the known data in literature on the vitamin-content of animal organs. For the titration 2:6-dibromophenolindophenol blue, which had been standardised against a known solution of ascorbic acid, was used. The tissue was weighed and minced with sand, and 1·5 per cent. trichloroacetic acid was added until the solution coloured thymol blue slightly red. The extract was filtered and titrated against the indicator to the first permanent trace of pink colour. On the whole, the determination seems to give reliable results, as the values obtained by this method are in fair agreement with biological tests. A few exceptional cases where the technique may be misleading are discussed. From the results obtained the following conclusions are drawn:—(i) The ascorbic acid content of the adrenals, based on 1 grm. of tissue, is much higher in every animal than that of the liver. (ii) The amount of ascorbic acid in the adrenals and liver is in fair agreement with the known antiscorbutic activities of these organs (Birch, Harris and Ray, *Nature*, 1933, **131**, 273; Mills, *Biochem. J.*, 1932, **26**, 704; Vedder, *The Military Surgeon*, 1932, **71**, 505). (iii) Certain animals, principally the rat and mouse, as well as the rabbit, are able to store ascorbic acid in the adrenals and liver, even if fed on a diet free from vitamin *C*. Dogs and cats were likewise able to do so when they were fed on meat which is relatively low in vitamin *E*. These results are likewise in agreement with those of Birch *et al.* (iv) Guinea-pigs fed first with liberal amounts of spinach, and then placed on a diet free from vitamin *C*, showed a decrease in the ascorbic acid content, first in the liver and then in the adrenals, indicating that the liver serves as a reserve store for the ascorbic acid. A

determination of the ascorbic acid content of the various organs of the guinea-pig showed that it is highest in the adrenal and lowest in the muscle, which is in agreement with previous knowledge. P. H. P.

Bacteriological

Decomposition of Pectin and Pectic Acid by Mould Fungi and Formation of Pectolytic Enzymes. S. A. Waksman and M. C. Allen. (*J. Amer. Chem. Soc.*, **1933, 55,** 3408–3418.)—Three of the mould fungi isolated from sand cultures of soil, *viz. Aspergillus niger, Penicillium sp.* and *Fusarium sp.*, proved so active in decomposing polyuronides and pectin that they were studied in detail. They attack polygalacturonic acid in different ways. *Penicillium* rapidly hydrolysed the polyuronide to simpler uronic acids, these in turn rapidly undergoing further decomposition. Although the complex precipitable by calcium chloride completely disappears within 7 days, it re-appears after that period, probably owing to synthesis, by the fungus or by its enzymes, of new complexes also precipitated by the calcium salt. *Aspergillus niger* decomposed the polyuronide and polygalacturonic acid more slowly than *Penicillium*, but no accumulation of hydrolytic products, *i.e.* simple uronic acids, occurred, these being rapidly decomposed into carbon dioxide, resulting in the liberation of energy which was utilised for the synthesis of larger amounts of fungus cell substance than in the case of *Penicillium*. *Fusarium* behaved like *Penicillium*, but the complete hydrolysis was slower. These mould fungi secrete pectolytic enzymes which effect the hydrolysis of pectin and of polygalacturonic acid, an increase of enzyme concentration resulting in a proportional increase in hydrolysis of the acid. It is proposed to define a unit of pectolytic enzyme as that amount of enzyme which will hydrolyse 1 mgrm. of polygalacturonic acid in one hour at 40° C., and at p_H 4·0 to 6·0. By this unit of measurement 1 grm. of a dry enzyme preparation of certain fungi contained about 4,000 pectolytic units. During the growth of the mould fungi in liquid cultures containing pectin or polygalacturonic acid, and, as a result of the action of the enzymes on these substances, a sediment is always formed, apparently containing either a lignin-like complex or a higher polyuronide not hydrolysed by cold 80 per cent. or by hot 5 per cent. sulphuric acid. D. G. H.

Organic Analysis

New Colour Reaction of Aldehydes. P. Rumpf. (*Compt. rend.*, 1933, **197,** 337–339.)—By treating one or two drops of an aldehyde in the cold with a few c.c. of a fresh solution of 2 to 3 mgrms. of rosaniline solution in 25 c.c. of 98 to 100 per cent. formic acid, it is possible to distinguish true aromatic aldehydes from those which, although possessing a nucleus at the end of an aliphatic chain, exhibit the properties often attributed to an enolic form. The absorption band of the yellow reagent has its maximum in the near ultra-violet and encroaches on the visible spectrum to about 4900 Å. Four principal cases arise: (i) Formaldehyde and chloral give immediately a restricted absorption band entirely in the visible region, the maximum being at 5480 Å, and the colour fuchsine-red for

formaldehyde. (ii) With aromatic aldehydes, and generally with those having the carbonyl group attached directly to a tertiary carbon atom (trimethylacetaldehyde), the colour changes little, but increases in brightness. For $\alpha\beta$-ethylenic aldehydes (excepting acrolein) the change in tint towards the orange is scarcely more marked. In either case spectrographic examination shows that the maximum of absorption may pass into the visible region beyond 4500 Å, and appears to correspond with mixtures, in varying proportions, of the original salt with compounds exhibiting a maximum at about 4800 Å. (iii) With all aldehydes with the carbonyl at a primary grouping, gradual recoloration in the green occurs, this being slow for the first two or three terms of the fatty series (max. 6270 Å). Addition of water leads to the successive separation of two weak bases: the first, which is violet (max. about 5600 Å), appears to be related to the soluble mauve colouring matter of Schiff's reaction, and the second, which is pure blue (max. about 5980 Å), is probably constituted analogously to Lauth's aldehyde blue. (iv) With acrolein (but not its β-substituted derivatives) and, in general, with all aldehydes having only one hydrogen atom in the α-position, the same reaction as in (iii) occurs, only more rapidly.

For polymerides, bisulphite derivatives and all products which, in a dry and acid medium, are able to yield fatty aldehydes, even in traces, the reaction is the same as with the corresponding aldehydes. Thus, trioxymethylene (insoluble in the reagent) and hexamethylenetetramine (soluble) act by dissociation like formaldehyde, paraldehyde and metaldehyde like ethanal, and chloral hydrate like chloral.

Systematic examination of 40 different aldehydes and other compounds has been made. Certain mixtures present difficulties, and application of the test to essential oils is complicated by the fact that some of the terpene constituents may undergo decomposition and yield the blue condensation product. T. H. P.

Presence of Formaldehyde in Terrestrial and Solar Atmospheres. N. R. Dhar and A. Ram. (*J. Indian Chem. Soc.*, 1933, **10**, 161–167.)—Formaldehyde (0·00015 to 0·001 grm. per litre) has been found in rain-water collected in India in June, July, August and September. Very small amounts of formaldehyde were found after heavy rainfall, and the larger quantities were present in rain occurring after a period of sunny weather. Freshly collected rain-water was used for the analyses, which were carried out by the iodine method (details not given). It is considered that the formaldehyde washed down by rain is formed in the upper atmosphere by the interaction of carbon dioxide and water vapour, under the influence of ultra-violet light, and the mechanism of the formation may be the reduction of carbon dioxide by atomic hydrogen liberated in the photochemical decomposition of water, the reduction process being stimulated by short-wave radiation. It is pointed out that the energy required in the formation of formaldehyde from carbon dioxide and water is practically the same as that required for breaking the hydrogen-hydroxyl link of water. Hydrogen present in the upper atmosphere is considered to hinder the photochemical decomposition of formaldehyde according to the equilibrium $HCHO \rightleftharpoons CO + H_2$. Since it has been shown (Dhar, *Z. anorg. Chem.*, 1932, **206**, 270) that several unidentified lines

in the solar spectrum agree fairly well with the absorption spectra of formaldehyde vapour, it has been concluded that formaldehyde may form one of the constituents of the absorbing atmosphere of the sun. S. G. C.

Japanese Beeswax. II. Composition of Free and Combined Fatty Acids. H. Ikuta. (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 377–379B; *cf.* ANALYST, 1931, **56**, 430.)—The sample of Osaka beeswax used in the investigation had the following characteristics: M.pt., 65°–65·5° C.; sp.gr. 100°/4° C., 0·8210; saponification value, 87·8; acid value, 7·5; ratio number, 10·7; iodine value (Wijs), 12·6; unsaponifiable matter, 56·3 per cent. with m.pt. 75°–75·5° C.; m.pt. of saponifiable matter, 47°–48° C.; neutralisation value of saponifiable matter, 195·5. The free fatty acids were isolated by dissolving the wax in a mixture of alcohol and benzene, neutralising with alcoholic potash, adding hot water, and boiling for a few minutes under a reflux condenser. The crude free acids were separated by boiling the soap solution with acid, ethylating in the usual way, and fractionally distilling. The results obtained showed that free acids in genuine Japanese wax represent about 4 to 6 per cent., and the combined acids about 38 to 41 per cent. of the original wax. After removal of the free acids, the residue was saponified by heating for 10 hours with *N* alcoholic potash, and, after removal of the alcohol, the residue was extracted with petroleum spirit to remove unsaponifiable matter, and the residual potassium salts were acidified with dilute hydrochloric acid, and the fatty acids were washed with hot water and dried. The combined fatty acids were then ethylated and distilled *in vacuo*. The eleven fractions were examined, and a hydroxy-fatty acid was found in the fatty acids recovered from fractions 5, 6, 7 and 8 (b.pt., 180°–200° C. at 2 mm.); this is being further investigated. The so-called margaric acid, found by Lipp in East Indian beeswax, was not present. About 60 per cent. of the combined fatty acids consisted of palmitic acid with some oleic acid, and two higher acids, $C_{26}H_{52}O_2$ and $C_{31}H_{62}O_2$, were also present both in the free and combined state; their chemical characteristics agreed approximately with those recorded for cerotic acid and melissic acid. D. G. H.

Manganese-Content of Some Australian Timbers. W. E. Cohen and A. B. Jamieson. (*J. Council Sci. and Indust. Res., Australia*, May, 1933, 116–119; *Division of Forest Products*, Reprint No. 11.)—Manganese is determined as follows:—From 5 to 10 grms. (according to the species) of oven-dried wood-splinters are ignited (in duplicate) in a platinum dish for 1 hour at 600° C. in a muffle-furnace provided with a good air-supply, the cool ash is moistened with water and a few drops of concentrated sulphuric acid, and 2 c.c. of hydrofluoric acid are added. The mixture is first warmed and then heated so as to remove the acids, and the process is repeated; if heating is stopped as soon as the fumes cease, silica, which occludes manganese (*cf.* J. Davidson, *J. Assoc. Off. Agric. Chem.*, 1931, **14**, 551), may be removed without the formation of insoluble oxides. The residue is then dissolved in a warm mixture of 2·5 c.c. of concentrated sulphuric acid, 0·5 c.c. of glacial phosphoric acid, and 10 c.c. of water, and the solution is transferred to a 100-c.c. beaker, sufficient water being used to ensure 50 c.c. of final solution (*i.e.* 6 per cent. acid; *cf.* M. B. Richards, ANALYST, 1930, **55**, 554). The colour obtained after boiling for 2 minutes with 0·3 grm. of potassium periodate, followed

by 25 minutes on the water-bath and then by cooling, is matched in a volume of 50 or 100 c.c. against that of a standard prepared in the same way from a known quantity of manganese sulphate, allowance being made for any blank given by the reagents. The results for Tasmanian myrtle (*Nothofagus cunninghamii*) show that manganese is present in varying quantities (ranging from 2 to 15 mgrms., expressed as Mn_3O_4 per 100 grms. of wood dried at 105° C.), although in any one tree the sapwood and intermediate wood always contained more than the true wood. No correlation of manganese-content with the colouring matter of the red type was found. Similar irregularities in quantities (1 to 40 mgrms.) were found with salmon gum (*E. salmonophloia*) and *E. crebra*, although in most cases the amounts found are considered more normal. The results should be expressed as described above, because figures given as a percentage of the ash are inconsistent and cannot be duplicated with any great measure of accuracy. Manganese is present in the numerous other eucalypts examined, but the quantities are too irregular for a quantitative determination to be used as a diagnostic feature (*cf.* ANALYST, 1932, **57**, 101). J. G.

Chemical Test for Distinguishing between the Woods of Hoop Pine and Bunya Pine. W. E. Cohen. (*J. Council Sci. and Indust. Res., Australia*, May, 1933, 126–127; *Division of Forest Products*, Reprint No. 13.)—(i) Five grms. of air-dry sample, rasped so as to pass a 20-mesh sieve, are heated for 3 hours under a reflux condenser with 50 c.c. of water, and the filtered extract, together with the 50 c.c. of boiling water used for washing, is cooled and diluted to 100 c.c. A layer of 1 c.c. of concentrated sulphuric acid is added to 2 c.c. of this extract in a roomy test-tube, and the mixture is then completed by gentle shaking; bunya pine (*Araucaria cunninghamii*) immediately produces a pink colour, followed (sometimes slowly) by an orange precipitate, whilst hoop pine (*A. bidwilli*) produces no colour, and a white gelatinous precipitate forms slowly. The appearance of the colour is the more trustworthy indication, but allowance must be made for the fact that extracts of bunya pine are usually more orange originally than those of hoop pine. Satisfactory results were obtained with 21 (out of 22) and 26 samples of the respective pines; the defaulting sample was similar to hoop pine in many ways, and is being further investigated. (ii) As a confirmatory test an extract in alcohol is prepared in a similar way, and a layer of 2 c.c. of concentrated sulphuric acid is added to a mixture of 2 c.c. of it with 5 drops of a 20 per cent. solution of diphenylamine in alcohol. The tube is shaken gently for 1 minute, when bunya pine gives a red-brown colour and hoop pine a light orange colour. Good results were obtained for 21 out of 22 and 23 out of 26 samples, respectively, the defaulting sample in the former case being the same as in (i). J. G.

Application of Selenium Catalyst in the Determination of Nitrogen and Phosphorus in Phospholipids. F. E. Kurtz. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 260.)—The selenium catalyst, as introduced by Lauro (ANALYST, 1931, **56**, 813) for the digestion with sulphuric acid in the Kjeldahl determination of nitrogen, has now been used in the determination of phosphorus; it reduces the time required in the digestion and avoids the customary nitric-sulphuric acid mixture, thus enabling nitrogen and phosphorus to be determined on the same

weighed sample. In the test experiments commercial egg-lecithin was digested with 20 c.c. of sulphuric acid, 5 grms. of potassium sulphate and 0·2 grm. of selenium; a clear solution was obtained in 15 minutes, and the digestion was continued for a further 15 to 20 minutes. The nitrogen was determined in the usual manner, and the residual liquid, after the distillation, was filtered to remove precipitated selenium; the phosphorus was precipitated as phosphomolybdate, after the addition of 30 grms. of ammonium nitrate, and finally determined as magnesium ammonium phosphate. S. G. C.

Inorganic Analysis

Precipitation of Metals of the Ammonium Sulphide Group. A. Krüger. (*Z. anal. Chem.*, **1933, 93**, 422–429.)—The process is based on precipitation of the feebly acid solution by hydrogen sulphide in presence of thiosulphate. *Separation of zinc from iron, nickel, and manganese.*—The solution is evaporated with a small excess of sulphuric acid for the complete removal of nitric acid; the residue is dissolved in 200 c.c. of water, and the solution boiled 15 minutes with 5 c.c. of strong sulphurous acid. After cooling, the liquid is neutralised with ammonia against methyl orange, and acidified with 1·5 to 2 c.c. of N sulphuric acid per 100 c.c. Hydrogen sulphide is passed at 70° C.; if no precipitate forms after 3 minutes, a few drops of sodium thiosulphate solution are added. When the bulk of the zinc has been precipitated the current of hydrogen sulphide is stopped, 1 to 2 grms. of thiosulphate are added, and the solution is cooled after a few more minutes. One-half of it is poured off, treated for 5 minutes with a slow stream of hydrogen sulphide, and added to the other half. The zinc sulphide may be collected after 5 hours. Cobalt is partly co-precipitated with the zinc, a greenish precipitate being formed; re-treatment is necessary.

Precipitation of iron and nickel.—The filtrate from the zinc sulphide is saturated with hydrogen sulphide and heated under pressure, after having been treated with 1 to 2 per cent. of ammonium chloride and enough thiosulphate to ensure precipitation of the iron. The sulphides are deposited in a pulverulent condition. If zinc has not been precipitated separately as above, it accompanies the other sulphides, the procedure forming a better group separation from the alkaline earths (owing to absence of carbonates) than the usual treatment with ammonium sulphide. The ferrous sulphide is easily washed, and on ignition gives oxide free from silica, a common impurity in precipitates produced by ammonia.

Precipitation of aluminium and chromium.—Precipitation by the above method (hydrogen sulphide under pressure in presence of thiosulphate) was found to achieve quantitative precipitation of aluminium and chromium hydroxides in a dense form. The application of the procedure to separations is under investigation.

W. R. S.

Determination of Bismuth in Copper. N. Kameyama and S. Makishima. (*J. Soc. Chem. Ind. Japan*, **1933, 36**, 364B–365B.)—A precipitate of manganese dioxide formed in the neutralised solution of a copper salt, which may contain chloride, may serve as a collecting agent for any bismuth present. The

sample of copper is dissolved in acid and the solution is neutralised, heated to 80° C., and treated with ammonia until a faint turbidity of copper hydroxide is produced, and a few c.c. of manganese sulphate solution (5 per cent.) are then added. The liquid is boiled, and 0·5 to 2 c.c. of *N* permanganate solution are added, drop by drop, with constant stirring. When the precipitate has coagulated, the same treatment is repeated, after filtering, "lest this precipitate should diminish the absorptive power of the manganese dioxide subsequently produced." The combined precipitates are dissolved, after filtering off, in dilute sulphuric acid containing a little hydrogen peroxide, the excess of which is then removed by boiling. The bismuth in the solution is determined colorimetrically by the iodide method, and it is emphasised that only a limited amount of sulphurous acid should be added to the colorimetric solution to reduce any iodine liberated, as an excess produces a yellow colour with iodide similar to that of the bismuth tetraiodide ion. Since there is some occlusion of copper by the manganese dioxide, a slight precipitate of cuprous iodide forms in the colorimetric liquid, and tends to occlude a trace of bismuth, which, however, may be recovered by reprecipitating the cuprous iodide after dissolving it in dilute sulphuric acid-hydrogen peroxide mixture. The method has been employed for amounts of bismuth up to 0·5 mgrm. per litre of copper solution; no test results are cited; it is stated that when only a few mgrms. or less of bismuth were present, more than 90 per cent. of it was collected by a single manganese dioxide precipitation. S. G. C.

Reagent for Copper, Cobalt, and Nickel. J. V. Dubsky and V. Bencko. (*Z. anal. Chem.*, 1933, **94**, 19–20.)—The reaction of copper salts with 1.2.diamino-anthraquinone 3-sulphonic acid (Uhlenhuth, *Chem.-Ztg.*, 1910, **34**, 887) is given by cobalt and nickel also, an intense blue coloration being produced. The colour due to copper changes to red, whilst those due to cobalt and nickel remain unchanged, on addition of ammonium chloride. The reagent is prepared from 0·5 grm. of the organic acid dissolved in 500 c.c. of water and 40 c.c. of caustic soda solution of 40° Bé. As little as 0·0019 mgrm. of copper in 1 c.c. still gives a blue tint. The chemistry of the reaction was investigated. The blue-black copper, nickel, and cobalt precipitates proved not to be of definite composition; the authors regard them as adsorption complexes, not as sulphonates or internal complexes. W. R. S.

Volumetric Determination of Bismuth. C. Mahr. (*Z. anal. Chem.*, 1933, **93**, 433–437.)—A new method is described, based on precipitation of the bismuth from bromide solution as yellow crystalline hexamminechromic hexabromobismuthate, distillation of the precipitate with alkali, and acidimetric determination of the ammonia in the distillate. W. R. S.

Determination of Small Amounts of Manganese in Salt Solutions. N. A. Clark. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 241–243.)—Willard and Greathouse's periodate method (*J. Amer. Chem. Soc.*, 1917, **39**, 2366) has been found satisfactory for determining manganese colorimetrically in amount down to 0·001 mgrm. in 50 c.c. of solutions of salts, such as potassium nitrate, magnesium sulphate, etc. The solution (50 c.c.), to which are added 5 c.c. of phosphoric acid

(85 per cent.) and 0·3 grm. of potassium periodate, is boiled for a few minutes, when manganese is converted to permanganate, and, after cooling, the colour is matched by the dilution method against a standard permanganate solution prepared by freshly oxidising, under the same conditions, a solution of known manganese-content. For testing ferric citrate, 0·1 grm. was ashed, and the residue was dissolved in dilute phosphoric acid. A blank test on the phosphoric acid used is advised. Feigl's benzidine reaction (*Mikrochem.*, 1923, **1**, 74), in which a blue colour is produced by the reaction of a benzidine salt with manganous hydroxide, was also tested, but it was concluded that, whilst it was satisfactory for qualitative purposes with as little as a few thousandths of a mgrm. of manganese, the colour tends to fade, rendering it unsuitable for quantitative work. S. G. C.

Reagent for Cobalt. H. Herfeld and O. Gerngross. (*Z. anal. Chem.*, 1933, **94**, 7–12.)—Cobalt solutions react with 1.2.nitronaphthol as with 1.2.nitrosonaphthol, yielding a red precipitate of the composition $[C_{10}H_6O(NO_2)]_3Co$. The precipitation is carried out in hot sulphuric acid solution; the precipitant is a 3 per cent. solution of the reagent in 50 per cent. acetic acid. After settling for some hours the precipitate is collected, washed with cold, then hot, 12 per cent. hydrochloric acid, and finally with water for the removal of chlorides. The ignition must be done with great care. The residual oxide is converted into, and weighed as, sulphate. Traces of cobalt may be determined colorimetrically; particulars are given in the paper. W. R. S.

Volumetric Determination of Cobalt by means of Ferrous Sulphate and Potassium Dichromate. L. A. Sarver. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 275–276.)—Willard and Hall's method (*J. Amer. Chem. Soc.*, 1922, **44**, 2219, 2237) consists in precipitating cobalt by means of a mixture of sodium hydroxide and sodium perborate as cobaltic hydroxide and determining this volumetrically in various ways. The use of a strongly acid solution of ferrous sulphate as a reducing agent gives results much too low, but by adding a weakly acid ferrous sulphate solution to the alkaline mixture in an air-free flask, subsequently acidifying with sulphuric acid, and titrating with potassium dichromate solution, quantitative results are obtained, even at the boiling temperature. The cobalt solution, free from interfering ions and containing at least 5 c.c. of 6 *N* sulphuric acid and 1 to 2 grms. of dissolved sodium perborate, is neutralised in a 500-c.c. Erlenmeyer flask with 6 *N* sodium hydroxide solution, and 10 c.c. are added in excess; black cobaltic hydroxide is precipitated and effervescence occurs. The mixture is boiled for 10 minutes to decompose the excess of perborate and to dispel oxygen; near the end of this period the flask is closed by a well-fitting rubber stopper carrying a dropping funnel (the tap being open). After removal of the flask from the source of heat, the tap is promptly closed, and an excess of standard ferrous sulphate solution is measured into the funnel. The tap is opened cautiously to allow the solution to be drawn into the flask, care being taken not to allow air to enter. The funnel is rinsed with two or three portions of water in a similar manner, the vessel is shaken for a few seconds, and 25 c.c. of 6 *N* sulphuric acid are admitted, whereupon the precipitate dissolves almost instantly. After the flask has cooled to room

temperature, the stopper is removed. About 10 c.c. of dilute phosphoric acid (25 per cent.) and 5 drops of aqueous barium diphenylamine sulphonate solution (0·2 per cent.) are added, and the excess of ferrous sulphate is titrated with standard dichromate solution to the appearance of a violet colour. Very accurate results were obtained in tests with 0·05 and 0·1 grm. of cobalt, with and without the presence of 20 to 40 mgrms. of nickel. Nitrates and other oxidising substances must be absent. Cobalt may be readily separated in one operation from manganese, chromium, vanadium, etc., by means of phenylthiohydantoic acid (Willard and Hall, *supra*); small amounts of iron, which are carried down with the cobalt precipitate, do not interfere with the method. S. G. C.

Colorimetric Determination of Iron as Thiocyanate. L. de Brouckère and A. E. Gillet. (*Bull. Soc. Chim. Belg.*, 1933, **42**, 281–293.)—As a result of a new study of the thiocyanate reaction of iron, made in an attempt to clear up some existing differences of opinion, the following conclusions were reached as regards the various factors influencing the method:—A considerable excess of potassium thiocyanate is necessary for the full development of colour, *viz.* 2·5 c.c. of a 50 per cent. solution for 25 c.c. of test solution, when, it is considered, the whole of the iron is converted into the highly coloured complex anion $[Fe(SCN)_6]^{- -}$. The colour is not affected by hydrochloric, sulphuric or nitric acid, provided that the concentration of acid is between 0·001 and 0·01 *N*; with hydrochloric acid, the concentration may reach 1 *N* without bad effect, but, with the higher concentrations, nitric acid produces intensification of colour due to interaction with thiocyanate, and sulphuric acid has a bleaching effect. It is of paramount importance that hydrolysis of the ferric salt should be avoided, since basic iron compounds interact very slowly with thiocyanate, and, therefore, any dilution of the iron solution should be done after, and not before, the addition of acid necessary to give the proper concentration at the higher dilution. The following, when present in concentration up to 1 grm.-equiv. per litre, were without effect on the colour: ammonium chloride, potassium chloride, potassium nitrate, magnesium chloride, calcium nitrate, barium chloride and aluminium chloride. Considerable amounts of manganese tend to cause high results, owing to the formation of a pink product; the positive error reached 18 per cent. when the manganese: iron ratio was 6000: 1. On the other hand, zinc and cadmium have a bleaching effect when present in concentration greater than 0·1 grm.-equiv. per litre. Phosphate ions, and, to some extent, sulphate ions interfere; it is recommended that if the concentration of sulphate ions is greater than 0·5 grm.-equiv. per litre, or if there is more than 1 grm.-equiv. of phosphate ions for 0·001 grm.-equiv. of ferric ions, a similar amount of these should be added to the comparison solution to compensate for the interference. The investigation was carried out with the aid of a plunger-type colorimeter, and an accuracy of 1 to 2 per cent. was obtained in the determination of from 5×10^{-5} to 1×10^{-4} grm.-equiv. of iron per litre, even when the iron-content of the comparison solution was 4 times as great as that of the test solution. Comparison should be made without delay, as the red colour is somewhat unstable.

S. G. C.

Rapid Analysis of Waterglass. F. S. Pertschik. (*Z. anal. Chem.*, 1933, **94**, 23–24.)—The customary evaporation with hydrochloric acid for silica may be avoided by the use of the following procedure:—The weighed sample (about 2 grms.) is mixed with 1·5 to 2 grms. of ammonium chloride and 15 c.c. of hydrochloric acid and heated on the water-bath for 10 minutes. After addition of 50 c.c. of hot water the precipitate is collected at once, washed with 3 per cent. hydrochloric acid, and ignited in a platinum crucible. After half an hour's ignition over a blast burner, the silica is weighed. W. R. S.

Microchemical

Micro-Density Determination of Gases by Direct Weighing. E. W. Blank. (*Mikrochem.*, 1933, **13**, 149–154.)—The density of gases is determined directly by weighing the gas in a small bulb of 8 to 10 c.c. capacity, on a microbalance to 6 places of decimals at known temperature and pressure, and comparing the weight with that of the same volume of water. The weighing bulb has a narrow neck, in which is a glass stop-cock grooved to prevent loss of tap grease, which would cause errors in weighing the bulb. The outside of the tip of the neck of the bulb is ground to connect with a double T-piece having two glass stop-cocks; this is used for filling and evacuating the bulb. To find the volume of the bulb it is evacuated, removed from the T-piece and filled by opening the stop-cock while the neck is in distilled water at room temperature. The tap is closed, the neck is dried, and the bulb is carefully wiped (the Pregl technique is used), left for half an hour and weighed against a similar bulb as counterpoise. The bulb is similarly treated when filled with the gas. The double T-piece facilitates filling with the gas, so that, if necessary, only one filling of the bulb may be carried out. If there is sufficient gas, it is best to fill the bulb with the gas, to exhaust and then refill the bulb, the operations being carried out in a thermostat, in which the bulb should remain for half an hour before wiping. The gas can readily be recovered for subsequent work, if necessary. Four determinations of the density of carbon dioxide gave a mean value 1·9788, as compared with the accepted value 1·9768. J. W. B.

"Spot" Tests for Ammonium Salts. F. Feigl. (*Mikrochem.*, 1933, **13**, 129–135.)—A drop of the test solution is placed at the bottom of a micro test-tube (Feigl, *Qualitative Analyse mit Hilfe von Tüpfelreaktionen*, Leipzig, 1931, p. 121), 2·5 by 1·0 cm., and covered with a drop of a 2 per cent. solution of sodium hydroxide. The test-tube is stoppered either with a ground-glass stopper with a hook on the under side, or with a one-holed rubber stopper through which passes a glass rod reaching nearly to the bottom of the test-tube. The reagent for testing the ammonia liberated is placed either on a paper hung on the hook, or in solution on a drop on the end of the glass rod. The test-tube is heated at 40° C. for 5 minutes on an asbestos plate, after which the apparatus is opened and the drop or paper is examined. The following reagents are used for testing the ammonia:—(i) *Litmus paper.*—The moist litmus paper is suspended on the glass hook; alkalinity, due to 0·1γ of ammonia, is easily recognised; as little as 0·01γ in

1: 5,000,000 dilution may be detected by comparing the tint of the litmus paper with a similar unused piece. (ii) *Mercurous chloride.*—A drop of a suspension of mercurous chloride is placed on the tip of the glass rod; when the test is completed, the drop is placed on a piece of filter paper, the darkening being visible with as little as 2·5γ of ammonia in 1: 20,000 dilution. (iii) *Nessler's reagent.*—A drop of Nessler's reagent is placed on the tip of the glass rod. When the test is complete, the stopper is removed and the drop is transferred to filter paper. A yellow colour is visible with as little as 0·1γ of ammonia in 1: 500,000 dilution. (iv) *Silver nitrate and formalin solution.*—The reagent is made from 10 c.c. of a 20 per cent. silver nitrate solution and 5 drops of a 40 per cent. formalin solution with a few drops of dilute sodium hydroxide solution, and the mixture is filtered from the precipitated silver. A drop of this is placed on the tip of the glass rod, and, after the test, examined on paper for reduced silver. As little as 0·05γ of ammonia in 1: 1,000,000 dilution can be detected. (v) *Silver nitrate and tannin.*—The reagent is made up from 5 c.c. of a 20 per cent. silver nitrate solution and 1 c.c. of a 5 per cent. tannin solution, allowed to stand for 24 hours, and filtered; it is freshly prepared for use. The test is carried out as (iv) above. As little as 0·1γ of ammonia in 1: 500,000 dilution can be detected. (vi) *Manganese sulphate (or nitrate) and silver sulphate (or nitrate).*—The reagent is made from 2·87 grms. of manganese nitrate, dissolved in 40 c.c. of water, filtered and mixed with a solution of 1·69 grm. of silver nitrate in 40 c.c. of water; the mixture is diluted to 100 c.c., and neutralised, drop by drop, with dilute sodium hydroxide until a black precipitate forms. It is filtered from this and kept in the dark. A piece of ash-free filter paper is impregnated with the reagent and placed on the glass hook of the apparatus. When the test is complete the slightly darkened filter paper is removed, and a drop of benzidine in acetic acid is added, a deep blue colour being formed with as little as 0·005γ of ammonia in 1: 10,000,000 dilution. J. W. B.

"Spot" Test to Distinguish Calcite and Aragonite. F. Feigl and H. Leitmeier. (*Mikrochem.*, 1933, **13**, 136–138.)—The test depends on the slightly greater solubility of aragonite in water, and the reaction of the hydroxyl ion formed according to the equations:—$CaCO_3$ (dissolved) $\rightleftharpoons Ca^{\cdot\cdot} + CO_3''$, and $2H_2O + CO_3'' \rightleftharpoons H_2CO_3 + 2OH$; and $Mn^{\cdot\cdot} + 2Ag. + 4OH' \longrightarrow MnO_2 + 2Ag + 2H_2O$ [see Test (vi), previous abstract]. *Reagent.*—Solid silver sulphate is mixed with a solution of 11·8 grms. of manganese sulphate ($MnSO_4 \cdot 7H_2O$) in 100 c.c. of water, boiled, cooled and filtered. One or two drops of dilute sodium hydroxide solution are added, and, after one or two hours, the mixture is filtered. The solution must be kept in the dark. *Procedure.*—A little of the powdered mineral is placed on a watch glass on white paper, or on a "spot" plate, and a drop of the reagent is added. If, after two minutes, a blackening is perceptible, aragonite is present; calcite will cause only a slight grey discoloration after 6 or 10 minutes.

J. W. B.

"Spot" Test for the Detection of Free Basic Oxides in Glass. F. Feigl. (*Mikrochem.*, 1933, **13**, 139–140.)—The reaction for hydroxyl ions, used as a test for ammonia, and to distinguish calcite and aragonite (see preceding abstracts),

is used to detect free basic oxides in glass. The manganese sulphate and silver sulphate reagent (see preceding abstract) is used, and a few mgrms. of glass powder are treated with a drop of this. The development of a gray colour, due to the reduced silver and manganese dioxide, indicates the presence of basic oxides; this may then be confirmed by placing the drop on filter paper impregnated with an acetic acid solution of benzidine, when a more or less deep blue colour is formed according to the amount of hydroxyl ions formed from the basic oxides.

J. W. B.

Micro-determination of Iodine in Eggs. H. J. Almquist and J. W. Givens. (*Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 254.)—To the liquid contents of a number of eggs are added an equal volume of ethyl alcohol (95 per cent.) and 10 grms. of potassium hydroxide for each egg, and the mixture is gently boiled under reflux for 16 to 24 hours. An amount of the dark brown liquid produced, equivalent to one egg, is evaporated to dryness in a 500-c.c. nickel or pyrex dish, and the residue is ashed at about 600° C. for 4 hours. The ash is extracted with 50 c.c. of hot water and filtered, and the residue is washed and rejected. The filtrate is neutralised to methyl red indicator with 6 N sulphuric acid, 5 drops in excess being added, and sufficient bromine water is added to give the liquid a strong yellow colour. The excess of bromine is boiled off, and the solution is evaporated to about 15 c.c. and transferred to a small separating funnel, any crystalline deposit being removed. A crystal of potassium iodide is added, and the iodine formed is extracted with five 1-c.c. portions of pure carbon tetrachloride. The iodine in the extract is determined colorimetrically against a standard solution of iodine in carbon tetrachloride. Corrections for the iodine-content of the reagents should be carried out, following the same procedure. Direct ashing of eggs without the alcoholic potash digestion was found to yield low results, owing to volatilisation of iodine. The method was tested on eggs to which were added 3 to 100γ per egg of iodine in the form of potassium iodide, iodosalicylic acid, or desiccated thyroid gland, and recoveries of very nearly 100 per cent. were obtained. Iodine-contents of 3 to 1750γ per egg have been obtained with untreated eggs.

S. G. C.

Physical Methods, Apparatus, Etc.

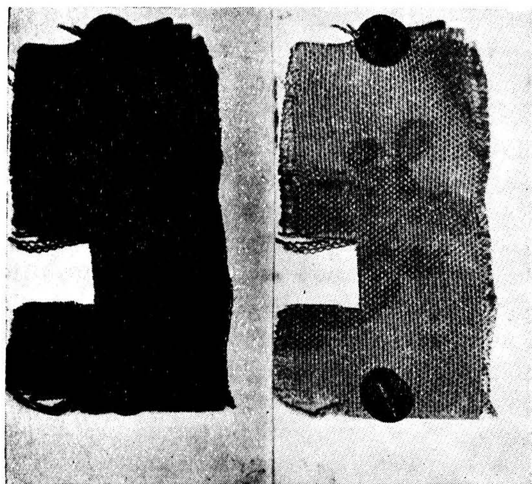
Determination of the Molecular Weight of Linseed Oil and its Polymerides. P. J. Gay. (*Chem. and Ind.*, 1933, **52**, 703–704.)—Proposed explanations of the variations with the concentration and the nature of the solvent observed in the cryoscopic method for the determination of the molecular weights of fatty oils are criticised (*cf.* Friend and Alcock, *J. Oil & Col. Chem. Assoc.*, 1924, **7**, 146; Morrell, *id.*, 1924, **7**, 153). It is concluded that, since neither association of the solvent molecules nor reaction between them and the solute completely explains all the discrepancies, it is possible that the deciding factor is the condition of the solvent at its f.pt. Thus (*e.g.*) with benzene as solvent the addition of oil breaks down the associated molecules, and thereby lowers the cryoscopic constant, whilst its effect on nitrobenzene (the viscous character and reactive nitro-group of which

suggest a different state of association) is in the reverse direction. Acetophenone (*cf.* Roy, *Compt. rend.*, 1932, **194**, 1356) is unsuitable, since its f.pt. falls on storage (particularly in the light), and there is some evidence that this is accompanied by a tautomeric change from the ketonic to the enolic form. Unsatisfactory results were also obtained with benzene, nitrobenzene and ethylene dibromide, and cyclohexane, which is chemically and physically inert, was therefore considered the most suitable solvent. It should be dried over calcium chloride and further purified by removal of traces of cyclohexanol by shaking with concentrated sulphuric acid, followed by distillation, recrystallisation 6 times, and a final drying; it then freezes sharply (within 0·001° C.) at 5·5° C. with little supercooling. Unlike most other solvents it shows little variation in cryoscopic constant with the concentration of the solute, values of 211·3 to 213·5 (mean 212·5) being obtained with concentrations of naphthalene ranging from 0·12 to 1·24 per cent. Values for the molecular weight of linseed oil were 876 to 880 for an acid-free oil dried over phosphorus pentoxide in a vacuum desiccator for several days (concentration 2·4 to 6·3 per cent.); 867·5 for the same undried oil at a concentration of 5·12 per cent.; 878 for commercial linseed oil (3·5 per cent.); and 1263 for the polymerides of this last oil at concentrations of 1·7 to 4·7 per cent. The values are constant within the limits of experimental error, and fall within those assigned by theory. Satisfactory results were obtained with polymerised oils of mean molecular weights as high as 4320, but in such cases the manipulative difficulties involve an error of 3 to 5 per cent. It is concluded that heat-polymerisation is fundamentally a chemical rather than a physical phenomenon. Polymerides have definite composition and molecular weight. J. G.

Radioactivity of Musts and Wines. E. Canals and A. Médaille. (*J. Pharm. Chim.*, 1933, **18**, 154–155.)—Previous work, in which the method of procedure is described (*cf.* ANALYST, 1932, **57**, 592), has been extended to wine-products from other districts, and similar degrees of radioactivity (0·05 to 0·25 millimicrocurie per litre) have been observed. Since the new wine was found to be more active than the corresponding must, an attempt was made to determine if any relationship exists between the degree of fermentation and the radioactivity, by comparing at 22° C. aerobic and anaerobic cultures of *S. ellipsoideus* with control cultures obtained in distilled water and in air. The radioactivity values in millimicrocuries were 0·048 to 0·108 for three filtered musts, 0·043 to 0·087 for the corresponding pulps, and 0·104 to 0·200 for the wines after 8 to 20 days of fermentation. Since the radioactivity of the wine is almost equal to the combined activities of the must and pulp, it is considered that no relationship exists between the radioactivity and the degree of fermentation, and that the earlier conclusions were due to the fact that the activity of the pulp was ignored. J. G.

Infra-Red Rays in Criminal Investigation. F. W. Martin. (*Brit. Med. J.*, 1933, 1025–1026.)—Attention is directed to the use of infra-red photography in the detection and demonstration of fresh blood stains. On the left is a photograph, taken in ordinary light, of a piece of blue serge cloth which was being examined for the presence of blood. No stain was visible either to the

naked eye or in the ordinary photograph. On the right is a photograph of the same cloth as it appeared when photographed with an infra-red plate. The stain revealed was proved to be blood by the usual microscopical, chemical and spectroscopic tests.*



* Dr. Martin informs us that the source of light used in taking the infra-red photograph was an ordinary bowl-shaped electric radiator. The plate was exposed for 30 minutes to the dull red glow from this, and was developed with amidol for 11 minutes. A more rapid method is to expose the infra-red plate to the light of a gas-filled lamp for 7 minutes, using the special filter supplied by the makers of the plates. Negative results were obtained with seminal stains, rust stains, and stains of old dried blood.—EDITOR.

Reviews

THE CONDUCTIVITY OF SOLUTIONS. By CECIL W. DAVIES, D.Sc. Pp. 291. 2nd Ed. London: Chapman & Hall. 1933. Price 15s.

The apparent failure of the law of mass action to apply to the ionisation equilibria of strong electrolytes led to a deadlock in the development of the theory of electrolytic dissociation originally proposed by Arrhenius. The introduction of the "physical theory" of Debye and Hückel, and its extension by Onsager, according to which strong electrolytes were supposed to be completely ionised—deviations from ideal behaviour being attributed to electrical forces of inter-ionic attraction—resulted, however, in a renewal of progress in this important subject. At first physical chemists were inclined to discard the Arrhenius theory of partial dissociation, except for weak acids and bases, and regarded salts as being always completely ionised; but in the course of time it became evident that this point of view was unsatisfactory and that the truth lay—as it generally does—somewhere

between the two extremes. It is now being realised, therefore, that the results to which the Debye-Hückel-Onsager theory leads must generally be modified by the individual properties of the electrolyte and the solvent; measurements of the conductivities of aqueous and non-aqueous solutions have contributed definite evidence towards the general acceptance of this concept.

It will thus be seen that the study of conductivity has played an important part in the development of the modern theory of strong electrolytes, just as it was fundamental to the introduction of the classical theory of electrolytic dissociation. With these facts in mind it will not be difficult to realise the importance at the present time of a monograph such as the one under review. The Debye-Hückel-Onsager theory has come to stay, at least for some years; it is the object of Dr. Davies in his book "to indicate the directions in which the older ideas (in connection with the theory of electrolytic dissociation) are being modified" as a result, and also to show how far the new concepts are in harmony with the old. It may be said at the outset that the author succeeds admirably in his task; the only criticism that can be offered is that the book is tinged very definitely with Dr. Davies' own point of view. This is, however, a good fault, for it is better to be given a clear lead than to be left in a welter of conflicting theories; since the author has himself contributed very materially to the development of the subject about which he writes, his ideas are worthy of serious consideration.

The book is divided into four parts: the first, entitled "Introductory," gives a short account of the inter-ionic attraction theory of Debye, Hückel and Onsager; this account is, perhaps, too short, but Dr. Davies anticipates criticism by "taking the view that the chemist will judge the equations not by the manner of their derivation, but by the degree of success with which they interpret and predict the results of experiment." The second and longest section of the book deals, therefore, with "Methods and Results," and in it the technique of conductivity measurements and the applicability to the results of the new theories are very clearly and critically discussed. The title of the third part is "Some Theoretical Applications and Consequences," which concludes with an important chapter on the "Dissociation of Electrolytes"; in this chapter the author gives an excellent review of theories of electrolytic dissociation, and includes an interesting theory of his own which aims at correlating the degree of dissociation of an electrolyte with the stability of the solvates the ions are capable of forming. The last section of the book, on "Analytical and Technical Uses," should prove of great value to analysts, particularly as the possibilities of conductimetric methods do not appear to be as widely recognised as they should be.

The book is written in a lucid and interesting manner; it has been well produced, and appears to be exceptionally free from misprints; only one of importance has been noted, *viz.* the word "phenol" in Fig. 31, which should, presumably, read "pyridine." Dr. Davies' monograph can be strongly recommended to all who wish to understand modern views on the ionisation of electrolytes; it is full of valuable data and stimulating ideas, although it should be read with a critical mind if its true value is to be appreciated.

S. Glasstone

The Science and Practice of Pharmacy. By R. R. Bennett, B.Sc., F.I.C., Ph.C., and T. Tusting Cocking, F.I.C., Ph.C. Vol. I. Pp. viii + 385, with 166 illustrations. Vol. II. Pp. vii + 339, with 72 illustrations and diagrams. London: J. & A. Churchill. 1933. Price 18s. each volume.

The authors of this work are so well known in the domain of manufacturing and pharmaceutical chemistry, and have such a wide practical experience upon which to draw, that these volumes are assured of a hearty welcome, which is not likely to be diminished by a study of their contents, for they are full of useful information, given in a concise and most interesting manner.

Vol. I, which deals with *Pharmaceutical Operations and the Manufacture of Pharmacopoeial Substances*, is divided into three sections: in the first, the principles involved in carrying out various pharmaceutical operations are explained, and the apparatus employed very fully described; the second covers the official galenical preparations of the Pharmacopoeia; and the third is devoted to a short account of the principles of the sterilisation of materials used in medicine, surgery and pharmacy. As is stated in the preface, "Manufacturing pharmacy is now essentially a branch of chemical industry and . . . necessitates a training in the elements of chemical engineering," so that it is not surprising to find in the first section a full description, with many illustrations, of almost all the ordinary processes employed in chemical engineering; in fact, this section might well serve as an introduction to the study of chemical engineering. Not only are the usual methods of grinding, mixing, evaporation and drying under ordinary and reduced pressure, filtration, distillation, expression and extraction clearly described, but there are also chapters on refrigeration, emulsification, the preparation of colloidal solutions and powders, crystallisation and sublimation, and osmotic pressure, including the preparation of iso-, hyper- and hypo-tonic solutions.

Section 2 gives a very complete description of the methods of preparation of the official galenicals of the British Pharmacopoeia, with explanations of the processes involved and of the reactions occurring during manufacture. This section shows most unmistakable evidence of the familiarity of the authors with the processes described, and abounds with hints and practical suggestions for obtaining satisfactory products. Whilst it should prove invaluable to the pharmacist, it will also be of considerable interest to those responsible for the analysis of such preparations.

In Section 3 the sterilisation of glass vessels and containers, and of solutions and oily liquids by chemical agents, heat, and filtration, is first described, and then follow three chapters on the preparation, sterilisation, and use of ampoules, injections, and vaccines and sera, together with methods for testing their sterility.

Volume II is devoted to the *Physical and Chemical Examination of Pharmacopoeial Substances*, and is essentially a commentary on the official tests and assays of the Pharmacopoeia. It is not intended to replace the Pharmacopoeia—indeed it could not do so, as full details of the analytical processes are not given—but it is complementary thereto. In publishing a standard method of analysis, there are two alternatives which may be adopted: either (i) to publish only the bare instructions how to proceed, or (ii) to include, with these instructions, the reasons

for each step to be taken. The latter course is that favoured by the Society's Standing Committee on Uniformity of Analytical Methods, but in the British Pharmacopoeia, possibly from considerations of space, the former method is adopted, and the object of this volume is to amplify the tests and assays of the Pharmacopoeia by explaining the rationale of the operations involved, together with the reactions taking place, and the necessity for the tests employed, owing to the origin or method of manufacture of the substance under examination. This task has been carried out in a most clear and efficient manner, similar substances being grouped together for consideration, and the explanatory matter accompanied by numerous equations and graphic formulae. Though this volume is intended primarily for the student, it cannot fail to be of interest to those who have to carry out the analytical processes of the Pharmacopoeia.

Both volumes are exceptionally free from misprints, and the authors are to be congratulated on the production of an extremely useful and interesting work, which is likely to become an almost indispensable associate of the Pharmacopoeia.

W. H. SIMMONS

HANDBUCH DER PFLANZENANALYSE. Edited by G. KLEIN. Vierter Band. Spezielle Analyse. Dritter Teil. Organische Stoffe III. With **121** illustrations. Erste Hälfte (pp. xii + 838). Zweite Hälfte (pp. vi + 1029). Vienna: Julius Springer. **1933.** Price, unbound, RM. **190.**

The two volumes under review constitute the two halves of Volume IV of this very extensive publication, portions of which have previously received notice in this Journal (ANALYST, 1931, **56**, 621).

The systematic description of the various groups of organic compounds occurring in plants, which was commenced in Volume II, is continued in this volume. The first half opens with a very excellent section of 176 pages on amino-acids by Dr. Winterstein, in which are described in considerable detail the characteristics of the various acids and the methods of isolating and determining them, including the use of flavianic acid and "Reinecke" salt, and the more recently introduced methods of colorimetric estimation of individual acids. Then follow sections on amides and amines, the latter containing an account of Müller's method of recovering bases from their rufianic or picric acid salts by adsorption of the acid upon wool, leaving the free base. A section of about sixty pages on proteins, written by Professor Bergmann and Dr. Zervas, gives a lucid account of the zymolysis of proteins and peptides, but only mentions, in passing, the valuable carbobenzoxy method of synthesing polypeptides devised by these authors. Some forty pages are devoted to the purines and allied compounds, and sixty or more to the nucleins. Professor Seka contributes a valuable section of some 220 pages on alkaloids, followed by a summary in tabular form of the occurrence of alkaloids of unknown constitution. A short section on cerebrosides, by the late Professor Thierfelder, completes the first half.

The second half, which is the larger of the two, contains monographs on ferments, antigens and antibodies, hormones and vitamins, thus completing the survey of organic plant constituents. Section III, entitled Special Methods, includes an account, by Professor Kofler, of biological methods of assay and a

description of the biochemical examination of natural waters. Other articles in this section deal with soil analysis (by Professor Ungerer), the examination of fermented solutions (by Dr. Maria Kobel and Professor Carl Neuberg), and the determination of the nitrogen distribution in plants and chromatographic adsorption analysis.

Section IV, consisting of about 300 pages, is devoted to tables giving the formulae and physical constants of all known organic constituents of plants, as well as of a number of salts and reagents mentioned in the text. There is a very complete index, which includes names of plants—a feature which greatly adds to its usefulness. The high standard set by the previous volumes is fully maintained, but one cannot help regretting that the price of this very useful book is so extremely high.

P. HAAS

HISTORY OF THE MICROSCOPE. By R. S. CLAY and T. H. COURT. Pp. xiv + 266. with 164 illustrations. London: C. Griffin & Co., Ltd. 1932. Price 30s.

The microscope is one of the very few scientific instruments bearing the rare distinction of a society honoured with a Royal Charter devoted entirely to its own development and use, and the reason for this eminence is evident in the pages of the present volume.

The original intention of the authors was to include the history of the modern achromatic microscope, but exigencies of space and cost *inter alia* have limited them to the period between that of the earliest magnifiers (about 1000 A.D.) and the earlier years of the nineteenth century, when the reflecting microscope was developed.

The text comprises the history of magnifiers described and used up to the invention of the compound microscope, apparently by Robert Hooke about 1665; this is followed by a chronological review of the latter instrument, in its numerous and highly varied forms, until efforts were made to overcome chromatic aberration by the use of concave mirrors instead of lenses. Such a compilation might readily have been resolved into nothing more than an ornate catalogue, but the authors have carefully avoided this by the introduction of brief notes of the makers and users of the instruments, quotations from old textbooks and other writings, trade cards, etc., and comparisons of the details of the various forms, so that, on the whole, the text makes interesting reading, and it is possible to peruse the volume from start to finish with pleasure.

The final pages of the book contain a list of over 300 English optical instrument makers of the seventeenth and eighteenth centuries, with details of their addresses, short biographical notes, and brief references to their outstanding productions. This is followed by complete and accurate "Names" and "Subject" indexes, which greatly enhance the value of the book. The text, in conjunction with the numerous excellent photographic illustrations, well demonstrates the diversity of form of the compound microscope and its accessories as produced by different makers, whilst the optical character of the instrument remained in practically the same form for over one hundred years. This elaboration was such that in several instances the actual use of the instrument as a magnifier was difficult and

quite subordinated to its production as a work of art, owing to the ornate decoration added. Adequate reference is made in this volume to the Continental makers, but it is evident that for many years the English manufacturers, and particularly those in London, were pre-eminent in the construction, not only of the microscope, but of other optical instruments also.

Without doubt the production of this work has involved an enormous expenditure of time and energy on the part of the authors, and their efforts have produced a notable contribution to microscopical literature, for it is certainly the most comprehensive book on the subject available. The interest of the text, the excellence of the illustrations, and the extreme care expended upon its compilation, commend this volume to all who are in any way interested in the history and development of the microscope.

T. J. Ward

The Vitamins in Health and Disease. By Barnett Sure. With a Foreword by Walter K. Eddy. Pp. xiv + 206. Baillière, Tindall & Cox. 1933. 11s. 6d.

Among biochemists the name of Dr. Barnett Sure, Professor of Agricultural Chemistry at the University of Arkansas, is well known (though perhaps still not as well known as it should be) for his work on the dietary requirements for fertility and lactation. During this work he discovered, simultaneously with Evans and Mattill, the anti-sterility factor, now called vitamin *E*, as first suggested by him. He also established the remarkable fact that 60 per cent. of the vitamin *B* ingested by the lactating rat is completely wasted as a supply for her sucklings. This second finding has implications in human pediatrics, as Dr. Sure himself and some of the leading American authorities on infant nutrition have frequently pointed out.

In spite, therefore, of the fact that Dr. Sure himself has no medical qualifications, it might be expected that his wide knowledge of vitamin work and its literature would equip him well for presenting to medical practitioners and students the bearing of that work on practical therapeutics and every-day dietetics. It can be justly stated that his book is a largely successful attempt to do this; in so far as it falls short of complete success, the fault is often not entirely the author's, but is due to uncontrollable circumstances.

After a short introductory chapter on "The Discovery of the Vitamins" the book continues with six chapters on vitamins *A*, B_1 (*B*), *C*, *D*, *E* and B_2 (*G*), respectively. It concludes with two chapters on "The Vitamin Content of Foodstuffs" and "The Rôle of the Vitamins in Health and Disease," and is supplied with author- and subject-indexes.

The footnote definitions of various medical, chemical, and other technical terms are an attempt to suit the book to the needs of students, "patients suffering from deficiency diseases," dietitians, nurses, and housewives. It is doubtful whether the combination of elementary exposition with historical and biochemical information can ever make a homogeneous and successful monograph, or at any rate one perfectly suiting the needs of each and all of these classes. For several of them—particularly the housewives and the patients (the latter victims of the former?)—Aykroyd's "Vitamins and other Dietary Essentials," reviewed some

months back (ANALYST, 1933, 428), would seem to tackle the problem on sounder lines. For students and dietitians, either the Medical Research Council's Report or Shermann and Smith's monograph, or both, might provide more detailed but equally intelligible information, particularly if selection is used in their reading.

Nevertheless, this volume does present a useful running account of each vitamin's history, and tells us, incidentally, a number of interesting facts that are often overlooked or forgotten. Theobald Smith's early discovery of experimental scurvy (in 1895), the very late recognition of the value of cod-liver oil in the treatment of rickets, the relative shortage of vitamin *D* in, or its complete absence from, most ordinary foodstuffs, and the fact that in 1930 there were 250,000 pellegrins (it is not clear whether the world or the United States is meant)—may be cited in illustration.

At the same time there are some rather strange omissions. The story of scurvy is brought up to the identification, by King, in Chicago, and Harris, of Cambridge, of vitamin *C* with hexuronic acid, but no reference is made to the simultaneous independent work, equally important, of Szent-Györgyi (Hungary) and Tillmans (Frankfurt a./M.). The preparation of calciferol (crystalline vitamin *D*) is attributed, in a footnote, to Windaus; no mention is made of the team of British workers at Mount Vernon, where the problem was independently solved, though both results were achieved and published no more recently than the work on hexuronic acid.

Most serious of all is Dr. Sure's complete failure to take cognisance of the international agreement, to which the United States were party, made in June, and published in October, 1931, about vitamin units and standards. This takes from his information about the vitamin-content of foods and practical methods of vitamin therapy much of its quantitative value.

This book will, unfortunately, be somewhat handicapped outside America, for two reasons. First, most of the information about foods applies only to the United States, and requires translating into terms of British (or European) dietaries, which can be safely entrusted only to the nutritional expert. Secondly, all the proprietary vitamin concentrates and preparations referred to in the text (and there are quite a number) are of United States origin, and, for the most part, not obtainable in this country. The English edition should be furnished with a suitable table of equivalents and information as to vitamin potency, in international units, where this can be obtained.

In spite of all that can be said in criticism of its plan or execution, the book remains one that can be recommended as a simple, interesting and substantially accurate account of vitamin work to date. It is quite free from the Americanisms that seem alternatively to infuriate or intoxicate many British readers (and writers), and the text appears blameless of typographical errors.

It must, in conclusion, be emphasised that Dr. Sure takes the orthodox, and therefore respectable, present-day view of the rôle of vitamins in practical medicine—that is, by prevention or cure, to make good dietary deficiencies. But the vitamins are all, to a greater or a less extent, substances with a high degree of physiological activity. The progress of the last few years has made it possible to-day to administer them at a level quite out of the question as long as they were

only available in foodstuffs where they normally occur at great dilutions. In relatively enormous doses they may show—evidence is not wanting that they indeed do show—pharmacological properties of an unexpected nature. They may, in that case, lend themselves to specific medical uses for treating conditions appearing at present quite unrelated with what we ordinarily call hypovitaminosis—a state due to deficiency of vitamins in the diet. In Dr. Sure's book there is not even a hint of this possibility. Yet it may be true, and, if it is true, it must be of outstanding importance.

A. L. BACHARACH

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DIE PRAXIS DER QUANTITATIVEN ORGANISCHEN MIKRO-ANALYSE. By A. FRIEDRICH. Vienna: F. Deuticke. 1933. Price M.7.

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WATER PURIFICATION CONTROL. By E. S. HOPKINS. Pp. x+131. Figs. 35. London: Baillière, Tindall & Cox. Price 10s.

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